LEVEL 12

Report

FINAL RESEARCH REPORT

on

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MECHANISMS OF PHOTOCHEMICAL
DEGRADATION IN XANTHENE LASER DYES

to

U. S. AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

February 20, 1981

by

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In the decade since its discovery, the dye laser has evolved into an exceedingly useful device, with applications in fields as diverse as analytical chemistry, spectroscopy, and isotope separation. While much progress has been made in the development of new and improved laser dyes, the performance of today's dye lasers is nonetheless compromised by the

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gradual photochemical degradation of the dyes during laser operation. The nature of the photochemical processes responsible for this degradation has remained largely unknown during the past decade, and thus the primary objective of this research program has been the detailed elucidation of the principal photochemical mechanisms which lead to the degradation of xanthene laser dyes.

The research performed in the course of this program has led to the discovery of an unprecedent excited state pathway for the photo-degradation of Kiton Red S, a sulforhodamine laser dye, in which the reactive, lowest energy excited triplet state of the molecule is populated by preferential intersystem crossing from upper singlet excited states, not from the singlet state nearest in energy to the triplet. The results obtained have also led to a tentative chronology of the first several stages in the photodegradation process, and have revealed the existence of a previously unknown contact charge transfer (CCT) complex between oxygen and methanol. While much remains to be learned about the details of the chemical reactions involved in the photodegradation of Kiton Red S and other xanthene dyes under various conditions, the research performed during this program has achieved significant progress toward this goal. In particular, enough has been learned about the degradation of these dyes that it is now possible to suggest new strategies for slowing their degradation under lasing conditions. These include, in particular, the removal of excitation wavelengths below 240 nm by selective filtering, and the use of improved triplet quenchers.

Several aspects of the photodegradation process remain incompletely understood. These include the detailed identity of the photo-degradation products formed from Kiton Red S and the other xanthene laser dyes, the role of peroxides in the photodegradation process, and the factors which result in the loss of lasing capability of dye solutions before appreciable degradation has occurred (as measured by chromatographic and spectroscopic analysis of the dye). We would suggest that these problems could form the basis for future research in this field, so the critical differences between lasing conditions and conventional irradiation conditions can be elucidated in more detail than has been possible to date.

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TABLE OF CONTENTS

LIST OF TABLES

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INTRODUCTION

In the decade since their discovery, dye lasers have evolved
from a laboratory curiosity to a large family of versatile, widely-used
sources of tunable, narrow-band, coherent visible light.[1,2] This rapid
development has been stimulated by the need for such light sources in
fields as diverse as analytical chemistry, spectroscopy, and, more re-
cently, isotope separation. Dye lasers are now commercially available
from several manufacturers, and it is clear that dye lasers have found
acceptance in an increasing variety of applications as their performance
characteristics have improved.

As useful as dye lasers have come to be, many problems remain to
be solved before they can realize their full potential. A particularly
vexing problem for many applications is the inevitable photochemical de-
terioration of the laser dye during the operation of a dye laser. This
deterioration occurs to a greater or lesser degree with all classes of
laser dyes, with the result that the efficiency of a dye laser typically

drops more or less continuously as the laser is operated. Laser action eventually ceases unless the dye is replenished.

A convenient measure of the useful lifetime of a given laser dye system is the total input energy (in Joules) which will produce a 50 percent decrease in the initial output of a given dye solution.[3,4] The units of "lifetime" are thus Joules/liter. It is typically found[4] that the laser dyes available today have lifetimes of 10^3 to 10^5 Joules/ liter, which corresponds to several hundred shots of a typical flashlamp-pumped dye laser. This corresponds to quantum yields for photodegradation on the order of 10^{-6} to 10^{-7}. Such dye lifetimes, while suitable for applications in which the dye solutions can be changed periodically, are unacceptably short for other applications requiring long-term stability of laser output.[4]

The problem of dye photodegradation in dye lasers has begun to receive increased experimental attention only during the past five or six years. Most of this recent work has concentrated (perhaps not surprisingly) on the measurement of rates and efficiencies of photobleaching of the dye, with relatively little attention having been given to the nature of the chemical processes involved. The studies which have been performed to date have been limited to two classes of laser dyes: the coumarins[3,5-7] and certain xanthene dyes, most notably the rhodamines.[8-20] In one study,[21] the effects of impurities on the laser performance of commercially-obtained laser dyes were examined.

It has been shown that, for coumarin laser dyes, the photochemically induced loss of lasing efficiency results from the formation of trace amounts of products which absorb strongly at the lasing wavelength.[5] Similar results have not been reported in the literature for other classes of laser dyes, although it has been reported that several (unidentified) products are formed during the lasing of Kiton Red S, a rhodamine-type dye.[4] It is further known that in the Kiton Red S system, the degradation of the dye is greatly accelerated by the use of a flashlamp which produces short-wavelength ultraviolet light in addition to

visible light.[4] Unfortunately, while the rate of photochemical degradation can therefore be reduced by the use of a cutoff filter such as Pyrex to eliminate the damaging ultraviolet radiation, the efficiency of laser operation is also significantly lowered by the introduction of the filter.[4] These observations have been confirmed in the course of Battelle's research in this area during the past three years.

Quite recently, a Russian study was published which claimed that the photobleaching of rhodamine dyes was accelerated by the presence of acids formed during the degradation process.[22] Our results do not support this contention, as will be discussed more fully in the discussion of program results. The formation of organic acids appears to be closely linked to the presence of dissolved oxygen in the dye solution. Thus, the use of oxygen as a means of quenching long-lived triplets which would otherwise give rise to degradation reactions or inhibit lasing by triplet-triplet absorbance,[1,2] may in fact produce its own set of adverse side reactions. As noted in our original proposal, a possible alternative to oxygen quenching might be xenon saturation, as xenon is known to be an effective, and certainly inert, triplet quencher.[23]

The photochemical behavior of the rhodamines and other xanthene dyes is still not clearly resolved in full detail, although much has been learned in the course of the present research program. The large majority of the studies which have been performed to date have dealt with rhodamine 6G lasers. Kato and Sugimura[17] have recently shown that under exposure to far-ultraviolet light from a low-pressure mercury/argon lamp, the bleaching of rhodamine 6G in methanol is **inhibited** by oxygen. They suggested that the oxygen reacts preferentially with the methanol (perhaps)
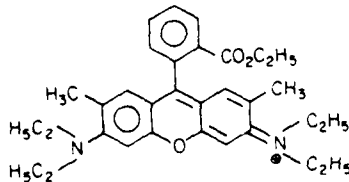
Rhodamine 6G

via the rhodamine-sensitized formation of singlet molecular oxygen) and
that a second process leads to photobleaching once the oxygen has been
consumed. One may speculate that this photobleaching results from
hydrogen abstraction by the triplet state of rhodamine 6G, since the pro-
cess does not begin until the triplet quencher (O_2) has been scavenged.
No real evidence for this pathway has been presented, however, beyond
several indications that the triplet state is in some way responsible for
photobleaching.[8,12,16] It has been shown that the photobleaching pro-
cess in rhodamine 6G is not biphotonic; the rate of bleaching varies lin-
early with the pump power both in fluid solution[11] and in solid ma-
trices,[14] ruling out the possibility of reactions between excited
states. Finally, other authors[13] have suggested that pH-dependent ag-
gregation effects in the dye solution may be responsible for some of the
observed losses in lasting efficiency.

The implication of triplet state reactions in the photobleaching
of xanthene laser dyes is reasonable despite the known very small quantum
yields of triplet formation (typically a percent or so[24] in rhod-
amines). Bimolecular singlet state reactions are unlikely because of the
short singlet state lifetimes (1-2 nsec[25]) these dyes exhibit. The
principal decay mechanism from the singlet state which is competitive with
fluorescence is radiationless decay, presumably due to the rotation of the
alkylamino end groups in those molecules for which this is possible.[24]
We have recently shown[26] that this radiationless decay is an activated
process having an apparent activation energy of 4-7 kcal/mole for both
rhodamine B and rhodamine 6G, with rate constants on the order of
10^7-10^8 sec^{-1} at room temperature. Interestingly, the triplet yield
is not detectably enhanced in rhodamine 101, for which rotational deac-
tivation of the excited singlet is not possible.[24,26]
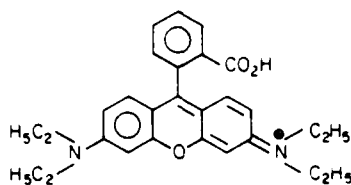
Rhodamine B
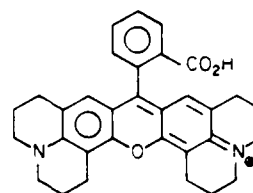
Rhodamine 101

The above observations raise a number of important and interesting questions about the role of upper excited states in the photochemistry of the xanthene dyes. While the detailed structures of the principal degradation products derived from the irradiation of xanthene dyes are still not known with certainty, our work during the past three years has succeeded in identifying the excited electronic states responsible for the degradation of Kiton Red S both in the presence and absence of oxygen. In addition, our results, together with those obtained by the group at Wright-Patterson Air Force Base,[4] have permitted us to formulate a tentative chronology of the initial stages of the photochemical degradation of Kiton Red S. These results are summarized in the following section.

We note in passing that some confusion has been allowed to persist in the literature with regard to the structure of Kiton Red S. The structure given by Drake, et al,[27] is in fact the structure of the well-known dye, sulforhodamine B[28]. There is, however, a well-characterized azo dye which is repeatedly referred to in the Color Index as Kiton Red S[29]. While we cannot speculate on the origin of this discrepency, we will continue to refer to sulforhodamine B (the compound we have been working with throughout) as Kiton Red S, in the interests of clarity and consistency.
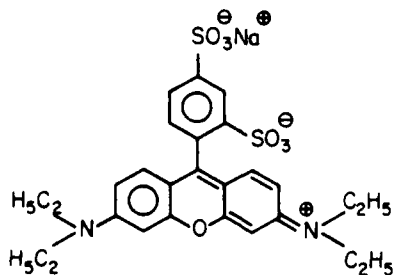
Kiton Red S
(Sulforhodamine B)
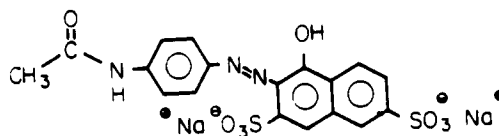
Kiton Red S
(Original Azo Dye Structure)

RESULTS AND DISCUSSION

The research performed in the course of this program has suc-
ceeded in providing a preliminary identification of the excited electronic
states responsible for the photochemical degradation of Kiton Red S (KRS),
and has in addition led to a postulated chronology of the initial stages
of degradation of KRS under continuous (not pulsed) irradiation condi-
tions. The mechanism so derived requires the unprecedented involvement of
upper singlet excited states in populating the reactive triplet states
which give rise to photo-degradation. Further, a previously unknown con-
tact charge transfer (CCT) complex between oxygen and methanol has been
discovered during this research program. This work has been performed in
close collaboration with the research group of Captain Sidney Johnson and
Dr. Ernest Dorko, at Wright-Patterson AFB, Ohio, whose group has been
actively involved in the study of the lasing properties of KRS. The col-
laboration has been quite valuable to all concerned. While several of the
details of the photochemical degradation process remain to be elucidated
(in particular, the identity of the degradation products and the rapid
loss of lasing output compared to the rate of photodegradation), the re-
sults obtained in this program have provided significant new insight into
the nature of the degradation reactions. These results are presented and
discussed in the following sections of this Report.

Experimental Materials and Apparatus

All of the dyes used in this research were obtained commercially
as laser-grade materials from Exciton, Inc. (Dayton, Ohio), and were
typically used as received. Solvents were "Distilled-In-Glass" spectro-
scopic-grade from Burdick and Johnson Laboratories (Muskegon, Michigan),
and were used as received. Other materials, such as sensitizers and
quenchers, were either purchased as high-purity reagent-grade materials or
were research gifts which were recrystallized prior to use.

Visible and ultraviolet absorption spectra were recorded on either a Cary Model 14M spectrophotometer or a Cary Model 17DX spectrophotometer. Infrared spectra were recorded on either a Perkin-Elmer Model 521 infrared spectrophotometer or a Digilab FTS-10 Fourier-Transform infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Varian CFT-20 Fourier Transform nmr spectrometer, while high performance liquid chromatography (HPLC) separations were conducted using either a 25 cm x 4.6 mm ID Lichrosorb RP-18 reverse-phase column (slurry-packed in our laboratory) and a mobile phase of 50% methanol and 50% pH 4.7 acetate buffer (0.1 M tetraethylammonium hydroxide, adjusted to pH 4.7 with glacial acetic acid), or a similar reverse-phase column with 30% aqueous acetonitrile containing 0.15 M triethylammonum bicarbonate (TEABC) as an ion-pairing buffer. The eluted components were detected optically at any of several wavelengths in the visible and ultraviolet spectrum. CW irradiations were carried out using a variety of standard cells and reactors, with a Varian-Eimac VIX-150, 150-W high-pressure xenon arc lamp having a high-UV rear reflector used for focused irradiations in spectroscopic cells, and a Hanovia 450-W medium-pressure mercury arc lamp used for preparative photolyses. A Phase-R Model DL-1200 UV flashlamp-pumped pulsed dye laser was used for the irradiations under lasing conditions.

Purity of Commercial Laser-Grade Dyes

Several studies in recent years have noted the importance of using rigorously purified laser dyes, and of verifying that the chemical structure of the dye as received commercially is in fact that which it is thought to be.[24,27] In particular, it seems to be the case that dye manufacturers have historically tended at times to substitute different chemical structures having the same color and dyeing properties in different shipments of a given dye.[27] While this practice does not usually pose any difficulties, it is of critical importance if one wishes to

perform careful photochemical studies of the photodegradation process. To positively establish the purity of our Kiton Red S, a rigorous high performance liquid chromatography (HPLC) investigation was undertaken. After numerous experiments were performed, a set of conditions was established that produced base-line separation of two colored components from the dye, with an approximately 10:1 ratio of peak heights.

A representative HPLC chromatogram, obtained with the acetate buffer as described in the preceding section, is shown below in Figure 1. Using a preparative-scale column of the same type, it has been possible to collect individual samples of the two components for examination by UV/Visible absorbance spectrscopy. The spectra so obtained are quite informative. As Figure 2 indicates, the two components have very similar spectra, with the main (visible) peak of Component 1 (the minor component) being blue shifted somewhat as compared to Component 2. Moreover, the spectrum of Component 2 is changed only slightly from that of an unchromatographed sample of Kiton Red S.

From the retention behavior of Component 1, and from the known synthetic procedure for making Kiton Red S,[28,30] it appears likely that Component 1 may be the mono-sulfonated derivative shown below. We suspect that this compound may also be a primary photoderadation product of Kiton Red S in the absence of oxygen. Further characterization of this compound has been hampered by the difficulty of isolating more than trace amounts of the material, even with preparative HPLC techniques, free of both KRS and the HPLC ion-pairing buffer. Thus, our attempts to identify the material by means of infrared or nmr techniques, or by elemental analysis, have not been fruitful. Because the role of this impurity in the lasing behavior and photodegradation of KRS is not clearly understood, it could be a useful topic for future study. Nonetheless, with the exception of this one impurity, the samples of KRS obtained for this research appear to have been adequately purified.
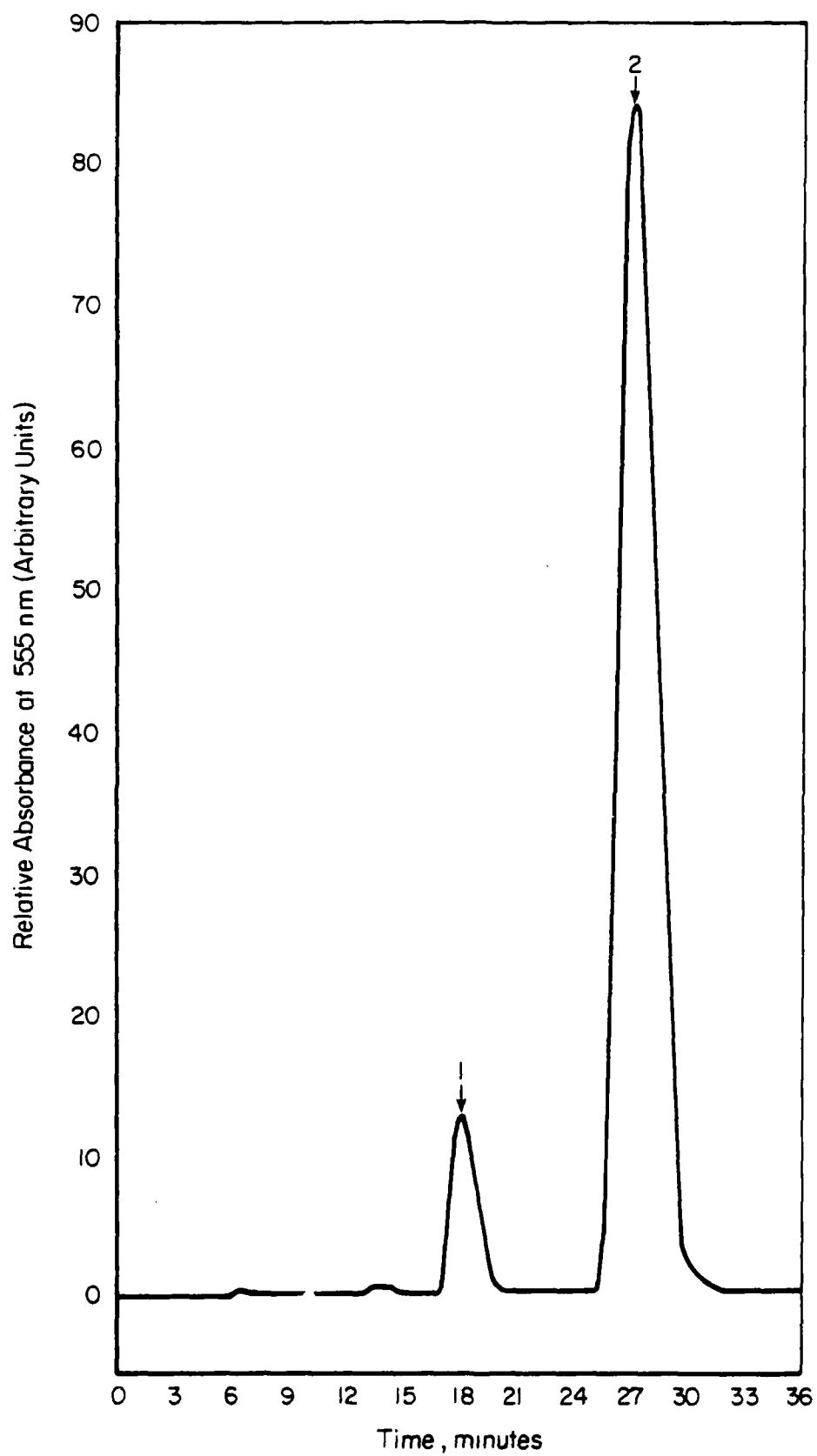
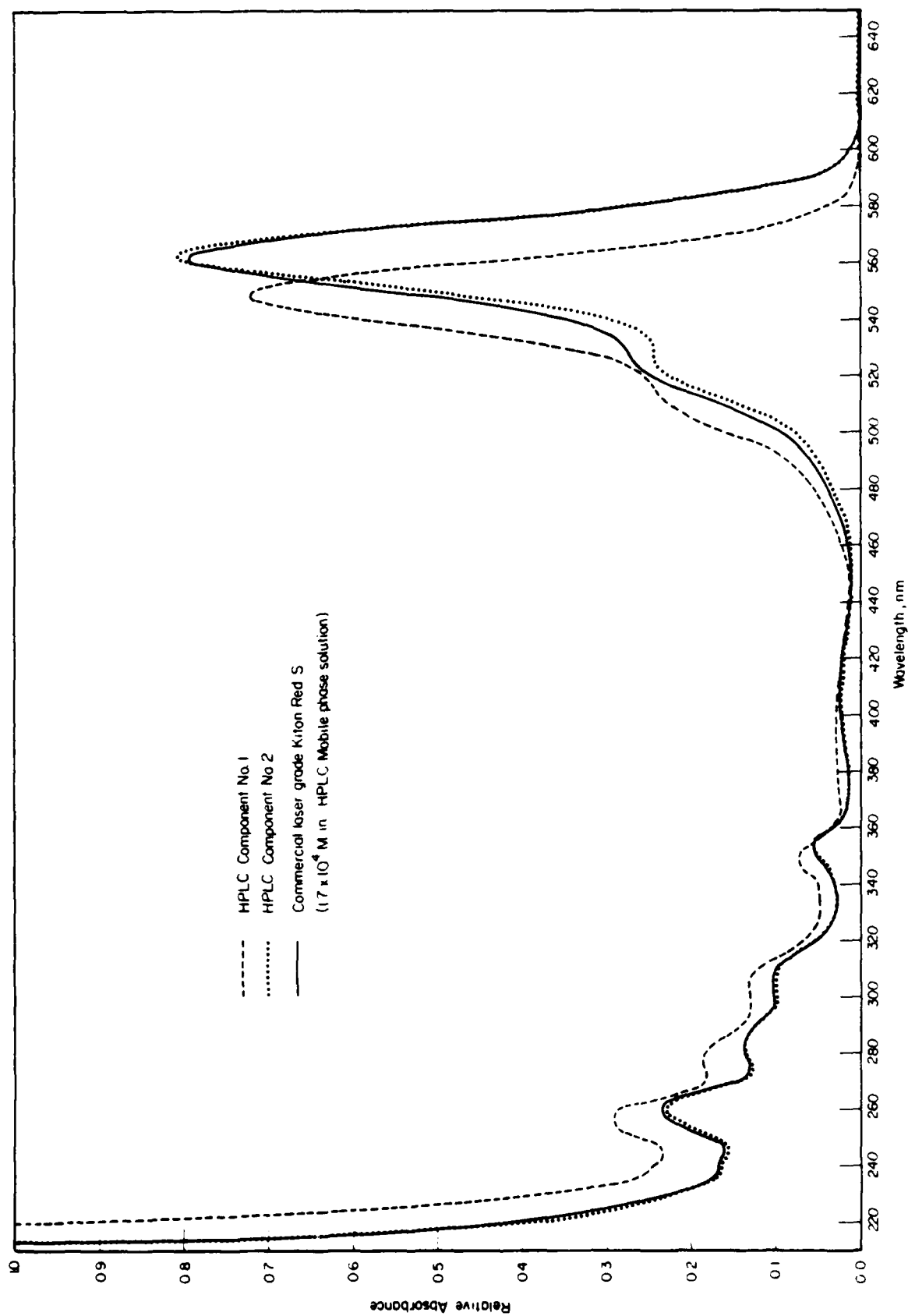FIGURE 1. REPRESENTATIVE HPLC SEPARATION OF THE TWO COMPONENTS IN COMMERCIAL KITON RED S

FIGURE 2. ABSORPTION SPECTRA OF COMMERCIAL LASER-GRADE KITON RED S AND OF THE
TWO COMPONENTS SEPARATED BY HPLC

H5C2 N
H5C2

SO3⊖

C2H5
N⊕
C2H5

O
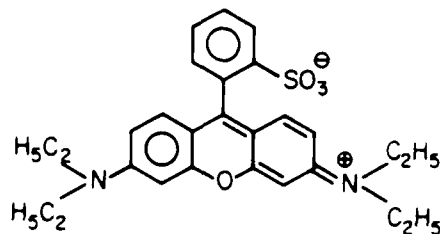
Postulated Structure for HPLC Component 1

(Sulforhodamine B)

Effects of Irradiation Wavelength

As we noted in our First Interim Report (March 10, 1978), one of
the most striking aspects of the photochemical bleaching of KRS in solu-
tion is its sensitivity to the wavelength of irradiation. The bleaching
reaction proceeds quite rapidly upon exposure to short-wavelength ultra-
violet light (below ca. 300 nm), and the interposition of a Pyrex filter
(which removes most of the light below ca. 290 nm) can extend the time
required for complete bleaching by a factor of 10 or more, depending on
the conditions used for the irradiation.[4]

We have observed that this wavelength effect is also reflected
in the spectroscopic properties of the dye. Thus, in the absorption
spectrum of KRS in methanol, for instance, the short-wavelength absorbance
bands (at ca. 240-300 nm) are nearly one-third the intensity of the main
(visible) absorbance band at 555 nm. In the fluorescence excitation
spectrum of the same solution, however (with the intensity of the visible
fluorescence band being monitored as a function of the excitation wave-
length) the intensity of the short-wavelength absorbance bands is only ca.
one-sixth the intensity of the main absorbance band. Thus, the short-
wavelength bands are substantially weaker in the fluorescence excitation
spectrum than in the absorption spectrum. This behavior is shown graph-
ically in Figure 3, below.

One may conclude from this observation that excitation into the
upper singlet excited states of KRS leads to less fluorescence than does
excitation into the lowest excited singlet state; that is, there is a
radiationless decay channel available to the upper singlet states which is
not available to the lowest singlet, and so the fluorescence resulting
from the relaxation of these upper singlets to the fluorscent state is
intrinsically weaker than that produced by direct excitation of the
fluorescent state. Since an increase in the rate of degradation is also
produced by the same short-wavelength ultraviolet light, these results
point to the intermediacy of a reactive upper excited state which is
formed by irradiation with ultraviolet light with wavelengths below ca.
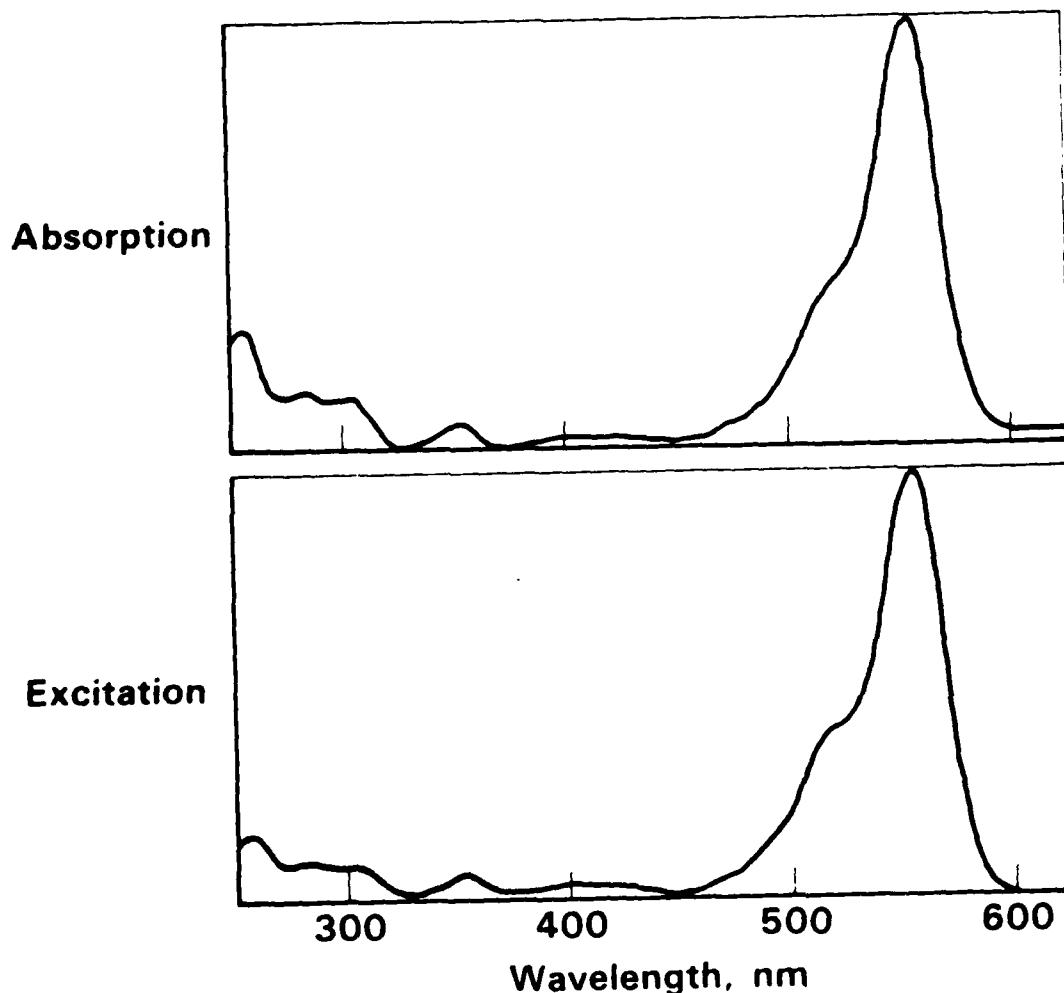300 nm.

FIGURE 3.   COMPARISON OF ABSORPTION AND FLUORESCENCE
            EXCITATION SPECTRA FOR KITON RED S IN METHANOL

This conclusion is dramatically reinforced by the results of a series of recent experiments, in which solutions of Kiton Red S in methanol and in water were irradiated with light selectively filtered so as to excited only well-defined portions of the absorption spectrum. These experiments were conducted by aligning two of the Elmac 150-W high-pressure xenon arc lamps fitted with quartz focusing lenses at right angles to each other, with the sample (contained in a 1.0 cm square quartz fluorescence cuvette) positioned at the point of intersection of the two beams. The appropriate filters could then be placed in either or both of the beams as desired. In this way, it was possible to excite (1) the visible band of KRS alone; (2) the UV bands from ca. 240 nm to ca. 410 nm alone; (3) both the visible and UV bands, using the above filter sets simultaneously; (4) the visible and UV bands together from ca. 220 nm to above 700 nm, by using a sharp cut far-UV filter; and (5) the entire absorption spectrum of KRS, including the weak, far-UV "tail" of the xenon arclamp spectrum below 220 nm, by using no filter at all.

The results are striking. As Table 1 indicates, the excitation of the UV bands above 240 nm, either alone or in parallel with excitation of the visible band, is not sufficient to produce rapid photodegradation. Only when the relatively low intensity light below 240 nm is used to irradiate the sample does the rate of photobleaching increase appreciably, with the most dramatic increase being observed only when the residual output of the xenon arc lamp below 220 nm was included. These observations argue strongly for the presence of a photodegradation pathway which can be accessed only by the excitation of upper singlet excited states having energies in excess of 120 kcal/mole, the energy corresponding to light having a wavelength of 240 nm. In the next section, we present evidence which serves to identify the nature of the excited states responsible for photodegradation.

TABLE 1. EFFECTS OF IRRADIATION WAVELENGTH ON RATE OF PHOTODEGRADATION

Sample	Irradiation Conditions	Lamp Output, %[a]	t_{90}[b]
6.75 x 10^{-5} M KRS in Methanol (Argon-Saturated)	Visible band only[c] (520nm-640 nm)	9.83	>10 hrs.
Ditto	UV bands only[d] (240 nm - 410 nm)	5.68%	>10 hrs
"	Visible bands plus UV bands[e] (240 nm - 440 nm; 520 nm - 640 nm)	15.51	~4 hrs
"	Full spectrum above ~220 nm (to 640 nm)[f]	25.01	~1 hr
"	Full spectrum above ~180 nm (to 640 nm)[g]	25.03	~10 min
6.67 x 10^{-5} M KRS in water (Argon-Saturated)	Full spectrum above ~220 nm (to 640 nm)[g]	25.01	~2.5 hrs
Ditto	Full spectrum above ~180 nm (to 640 nm)[g]	25.03	~10 min

(a) Percent of total spectral irradiance for the wavelength range indicated, from manufacturer's data for the Varian Eimac VIX-150 high-pressure xenon arc lamp.

(b) Time required for 90% photodegradation to occur, as monitored by the height of the visible absorption band.

(c) Corning CS 3-69 filter plus Corning CS 4-94 filter, single lamp.

(d) Corning CS 7-54 filter, single lamp.

(e) Filter set (c) on Lamp 1 plus filter (d) on Lamp 2.

(f) Corning CS 9-54 filter, single lamp.

(g) Unfiltered output, single lamp.

Effects of Oxygen Saturation

There appear to be several effects of oxygen on the photochem-
istry of the KRS—methanol system. There is, first of all, a pronounced
__increase__ in the time required for complete bleaching to occur in the
presence of oxygen. Under conditions of complete oxygen saturation (with
the gas being bubbled through the solution continuously, with stirring,
during the irradiation) the presence of oxygen increases the time required
for complete bleaching by nearly a factor of 10. The photobleaching of
KRS is linear in time under conditions of both oxygen saturation and argon
saturation, so long as the solutions are purged continuously, and thus
continuously saturated, with the gas under consideration. The rate of
bleaching is roughly the same in the presence of air and of pure oxygen,
and is independent of the concentration of KRS. This behavior is illus-
trated by the visible absorption spectra shown in Figures 4 and 5. These
experiments were conducted using the immersion— type photochemical reactor
and mercury arc lamp shown schematically in Figure 6, with the atmosphere
inside the reactor controlled by bubbling either argon, air or oxygen
through the solution of KRS prior to, and in some cases during, the ir-
radiation. Aliquots of the solution in the reactor were withdrawn at the
intervals noted for spectroscopic analysis. It is clear that under these
conditions (with the gas being bubbled through the solution continuously,
with sitrring, during the irradiation) the presence of oxygen increases
the time required for complete bleaching by about an order of magnitude,

Further, there is an obvious perturbation of the chemistry in-
volved. As Figure 4 indicates, the bleaching of an argon-saturated solu-
tion is accompanied by a noticeable color change, from the original
reddish-pink of fresh KRS to a bright orange color, before the solution
becomes colorless. This corresponds to the slower dimunition of the
shoulder at __ca.__ 520 nm than the main band at 555 nm. In oxygen-saturated

PHOTOBLEACHING OF KRS IN ARGON-SATURATED METHANOL (continuous purge)

Initial concentration ~ 8 x 10^{-5} $\underline{M}$

Prior to irradiation

Total irradiation time
5 min ($\frac{1}{12}$ hr)

Total irradiation time
50 min ($\frac{5}{6}$ hr)

Total irradiation time
105 min ($1\frac{3}{4}$ hr)
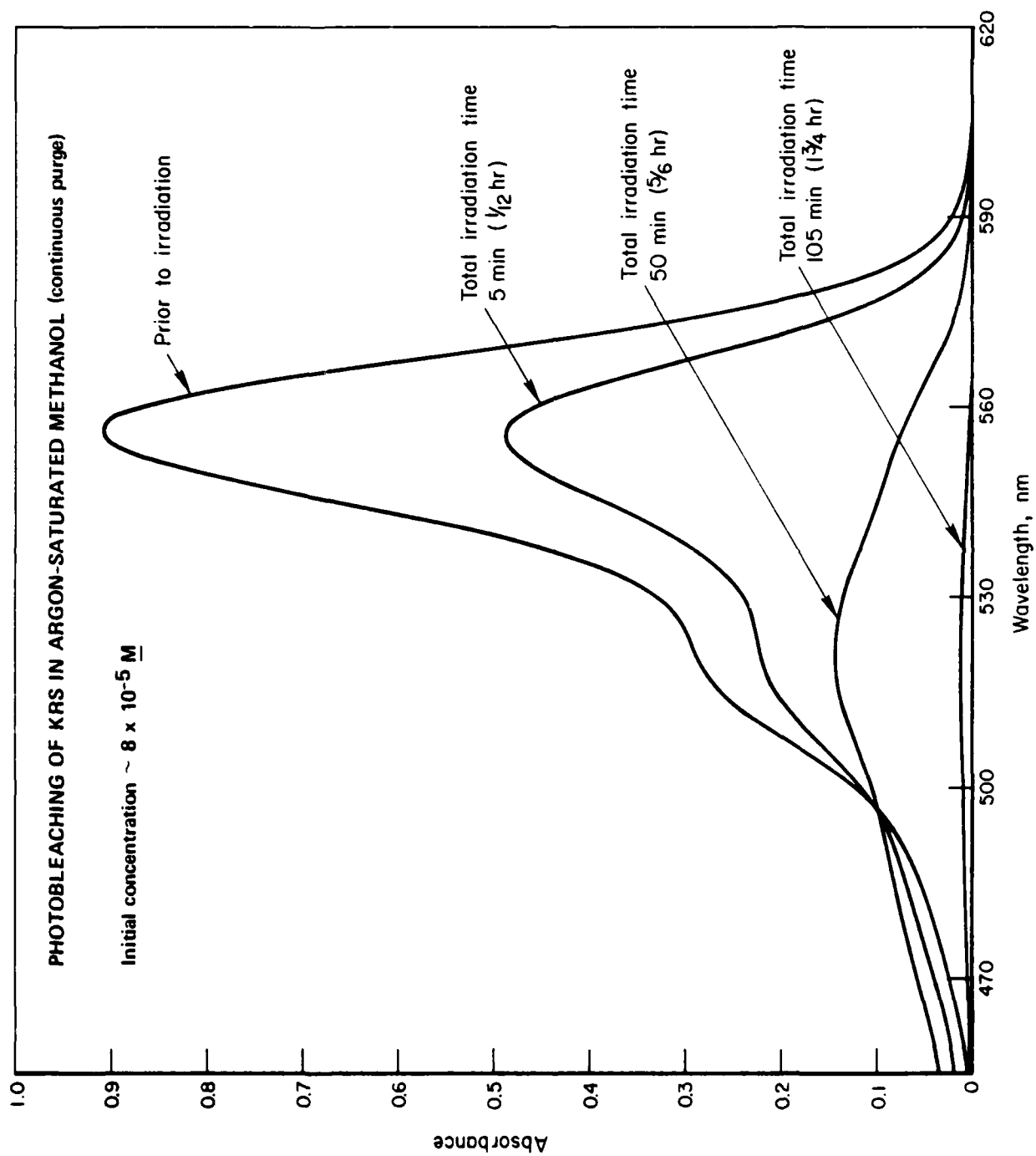
Absorbance

Wavelength, nm

FIGURE 4. PHOTOBLEACHING OF KRS IN ARGON-SATURATED METHANOL (CONTINUOUS PURGE)
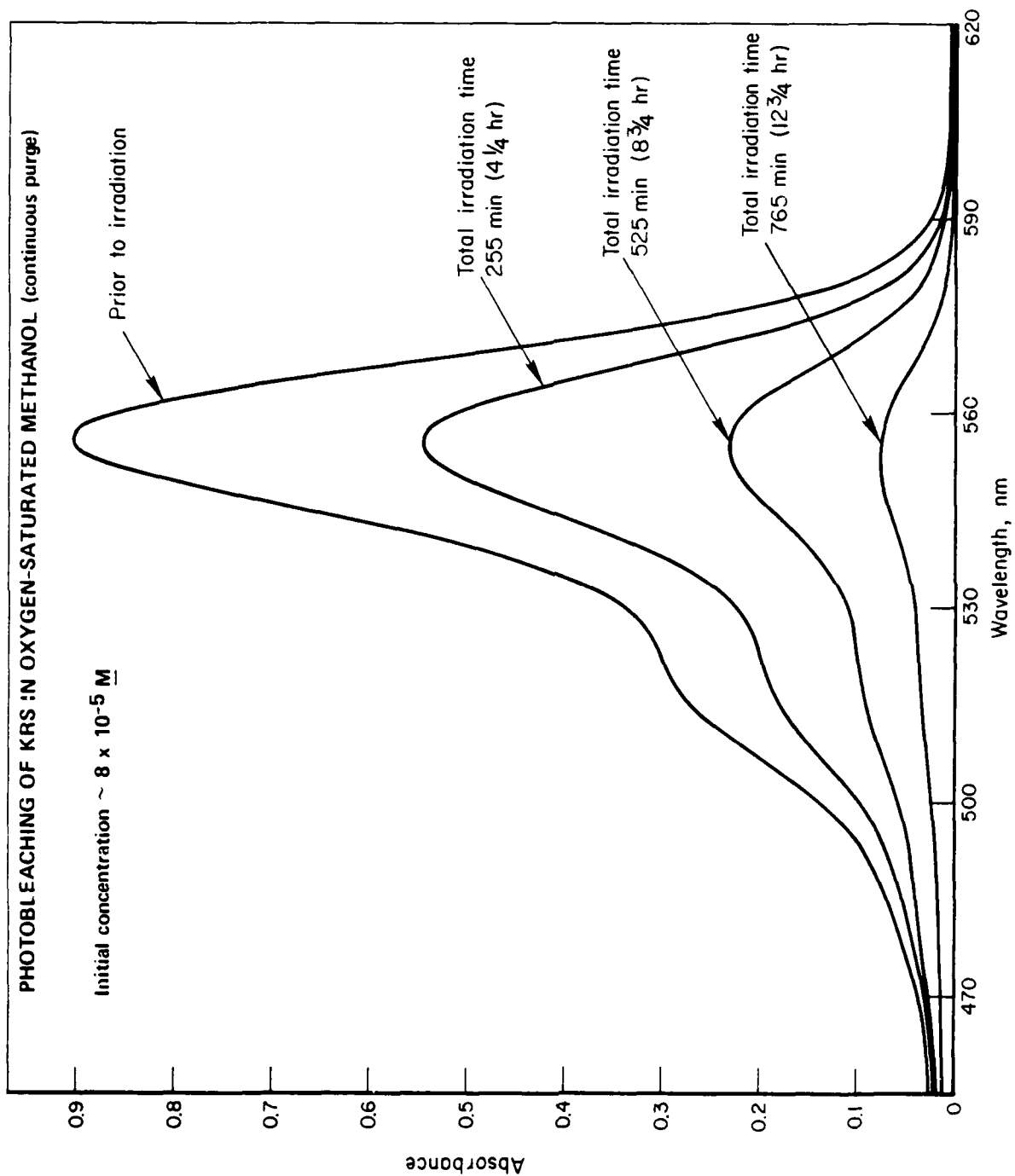
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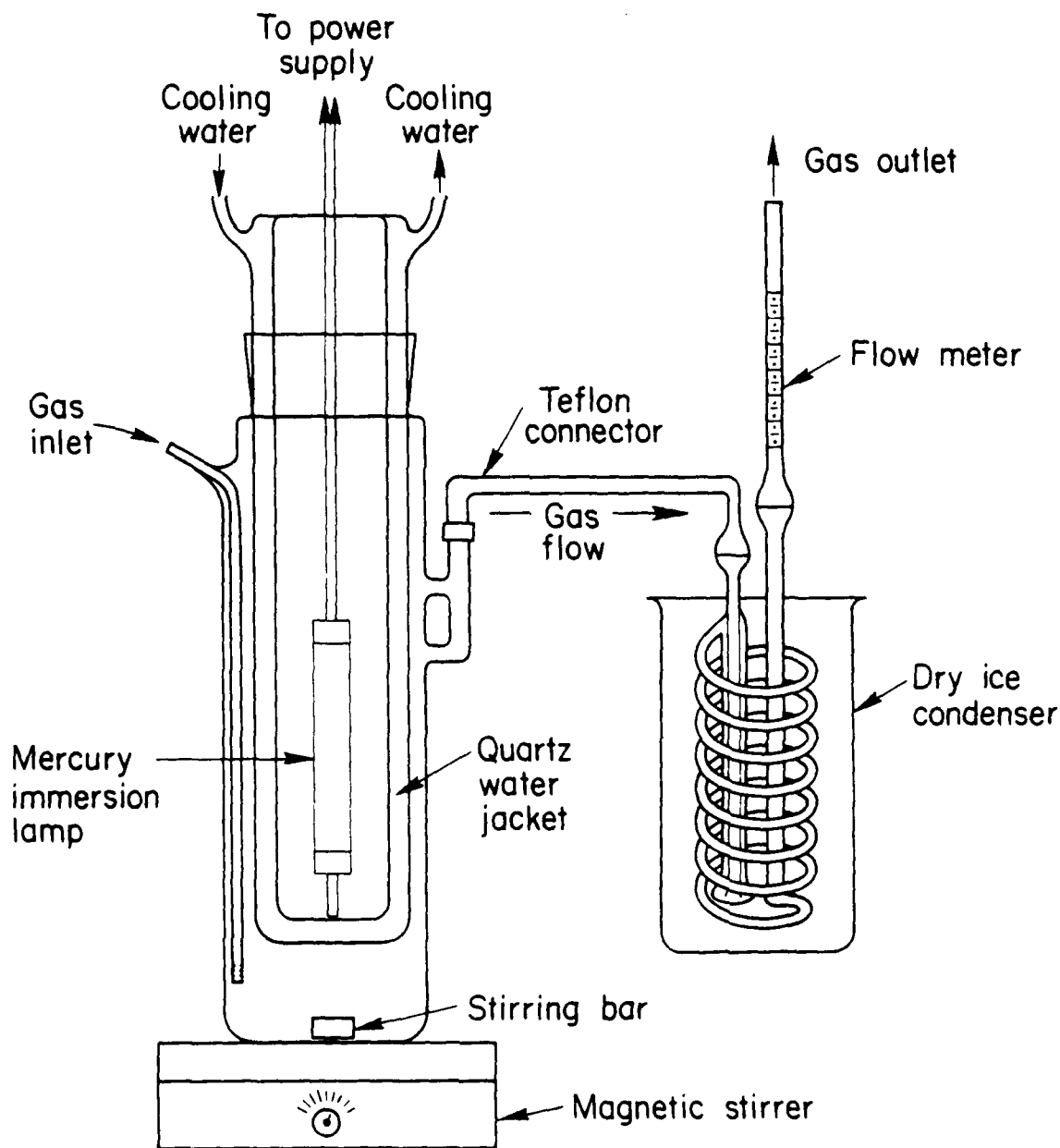FIGURE 5. PHOTOBLEACHING OF KRS IN OXYGEN-SATURATED METHANOL (CONTINOUS PURGE)

FIGURE 6. SCHEMATIC ILLUSTRATION OF PREPARATIVE-SCALE
PHOTOCHEMICAL REACTOR

solutions, no such color change is observed; as Figure 5 shows, the entire spectrum bleaches uniformly.

This change in chemical pathway is manifested in other ways, as well. For example, in experiments where gas were trapped in a dry-ice condenser as shown in Figure 6, it was noted that the products from argon-saturated solutions smelled strongly of mercaptans (but not of hydrogen sulfide), suggesting that extensive reduction and cleavage of the sulfonic acid groups of KRS had occurred. In oxygen-saturated solutions under the same conditions, no sulfurous smell could be detected at all; rather, these solutions had a pleasant odor suggestive of a mixture of low molecular weight organic carboxylic acids and esters. Even these mixtures of volatile products (which, incidentally, should have contained relatively few secondary photochemical products) were so complex that analysis has proven difficult. Approximately 15 trapped, volatile components have been observed by gas chromatography, with many more components being present in the remaining product-containing solutions. More than a dozen compounds, which are likely candidate degradation products, have been chromatographed in an attempt to identify the products formed. No matches have been found, however, between the chromatographic retention times of the authentic compounds and the components of the degradation mixtures. Our efforts to identify the products of photodegradation will be discussed more fully in a subsequent section of this report.

The effect of oxygen on the rate of photobleaching is shown more quantitatively in Figures 7 and 8. Figure 7 indicates that the photo-bleaching of KRS is linear with time in both oxygen and argon so long as the solutions are purged continuously, and thus continuously saturated, with the gas under consideration. Further, it can be seen that the rate of bleaching is roughly the same in the presence of air and pure oxygen, and is independent of the concentration of KRS.

A different pattern is observed in static systems, in which the flow of gas is stopped after saturating the solution (but prior to irra-
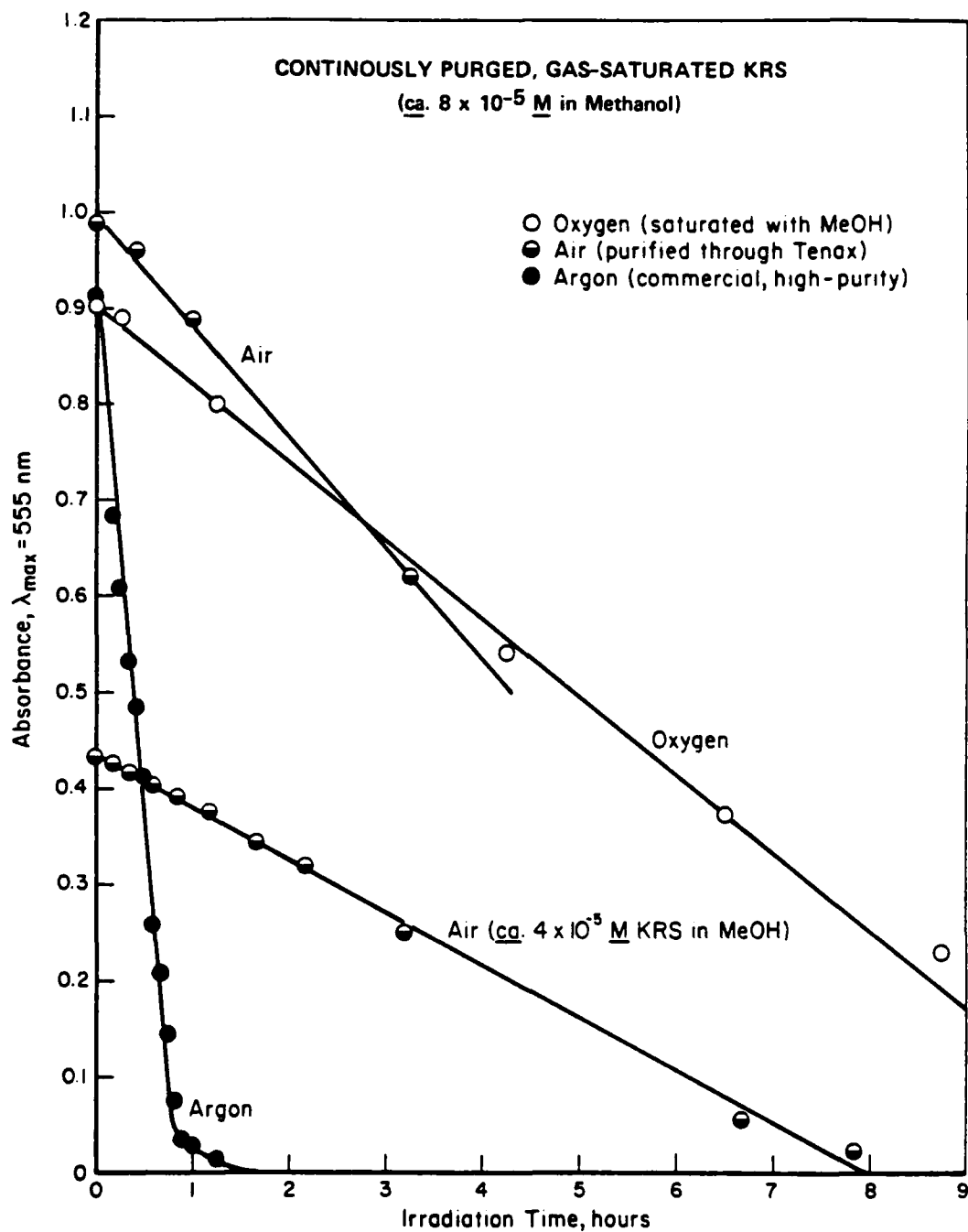
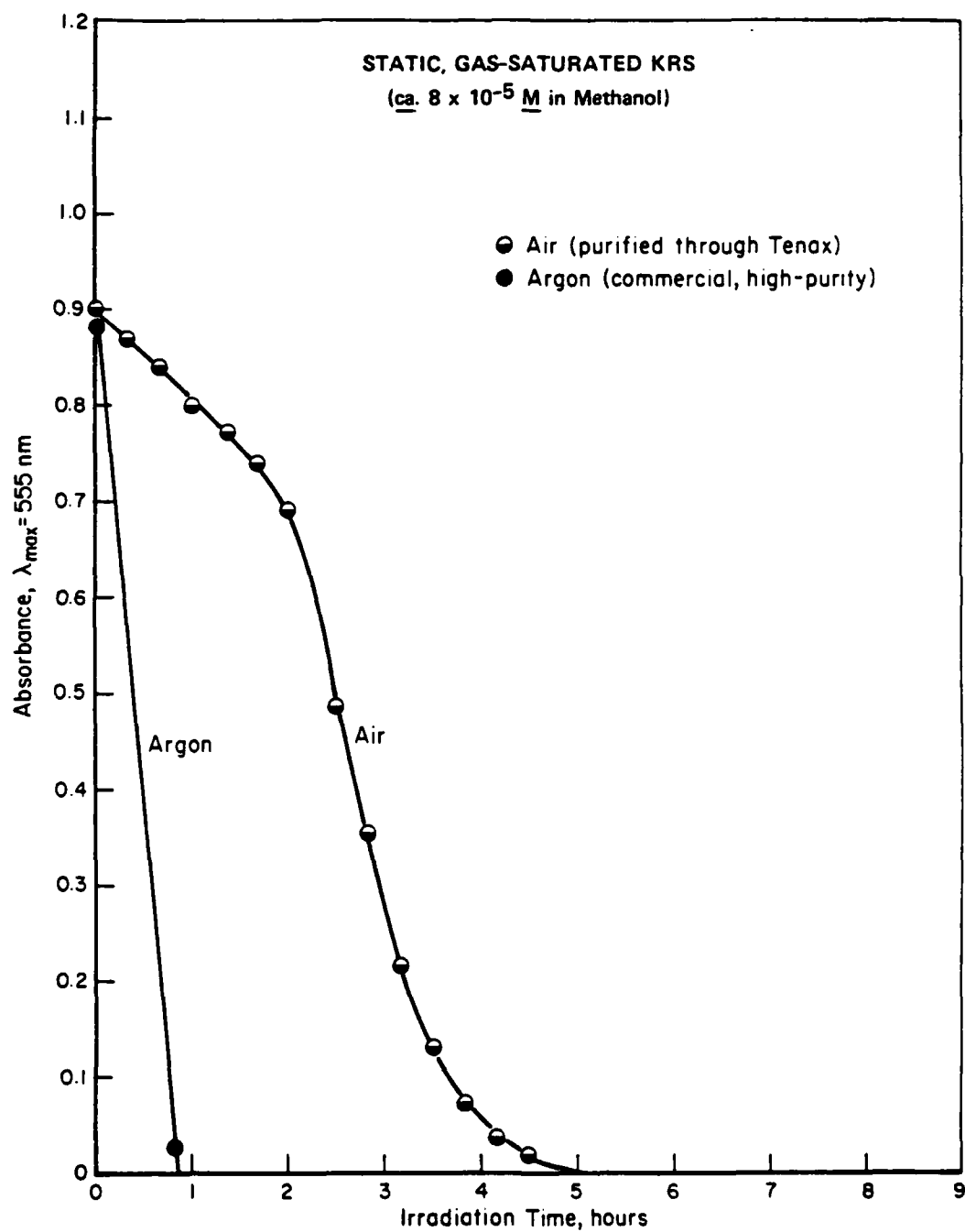FIGURE 7. RATES OF PHOTOBLEACHING OF CONTINUOUSLY PURGED, GAS-SATURATED KRS IN METHANOL

FIGURE 8. RATES OF PHOTOBLEACHING OF STATIC, GAS-SATURATED KRS IN METHANOL

diation). As Figure 8 indicates, the bleaching reaction is still very rapid in argon, but the air-saturated solution now exhibits non-linear bleaching. This puzzling behavior is more easily understood when the two sets of data are combined, as in Figure 9. It can be seen that the rate of bleaching under argon is unaffected by the change from continuously purged to static conditions. In the presence of air, it can be seen that the photobleaching of the static system proceeds initially at the same rate as in the oxygen-purged system. This may be thought of as the oxygen-limiting rate of bleaching. Then, when the oxygen present in the static system has been consumed, the rate of bleaching increases until it is essentially the same as the argon-saturated rate. This may therefore be thought of as the intrinsic rate of photobleaching. Thus, it is clear that while oxygen retards the rate of photobleaching by roughly an order of magnitude, it does so with an accompanying perturbation of the photochemical processes which occur, resulting in irreversible reactions which scavenge the oxygen present in the solution.

Another series of experiments was conducted to explore the photodegradation of KRS solutions using our Phase-R model DL 1200 UV co-axial flashlamp-pumped dye laser. This apparatus is shown schemically in Figure 10. The results of these experiments, continuously bubbling either argon or air through the solution during the photobleaching, are summarized in Figure 11. The rates of degradation and the times when lasing ceased were nearly identical for both the argon-saturated and the air-saturated solutions of KRS in methanol. This kinetic behavior is strikingly different from that observed with the immersion apparatus. In particular, the similarity between the air-saturated and argon-saturated photobleaching experiments may be due to incomplete degassing of the system with argon, although precautions were taken to minimize this problem. The nonlinear behavior of these systems is perplexing, and is not well understood. It should be pointed out, too, that in these experiments we observed recovery of lasing in solutions that had previously ceased lasing, after they were allowed to stand in the dark for several days. This
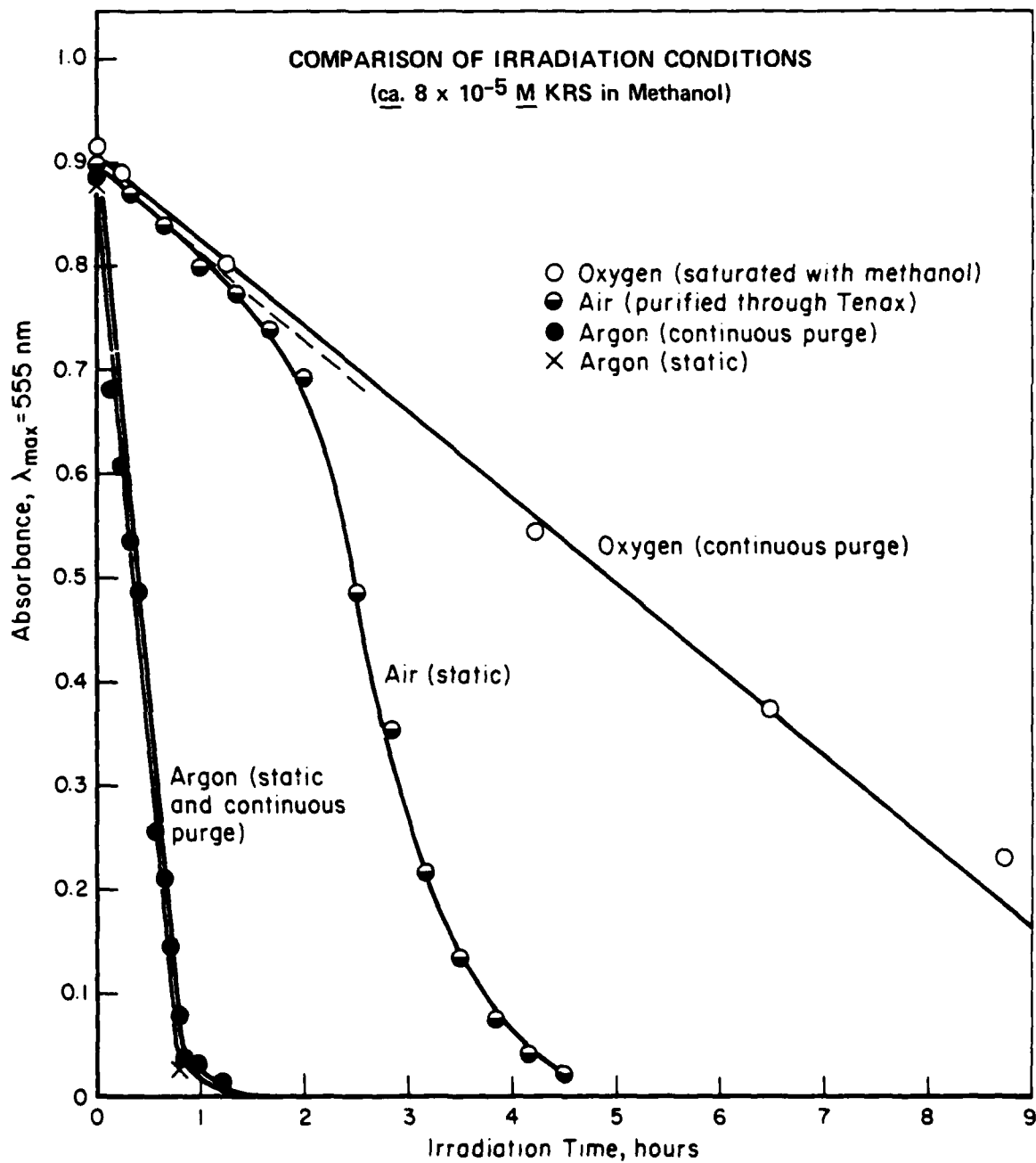
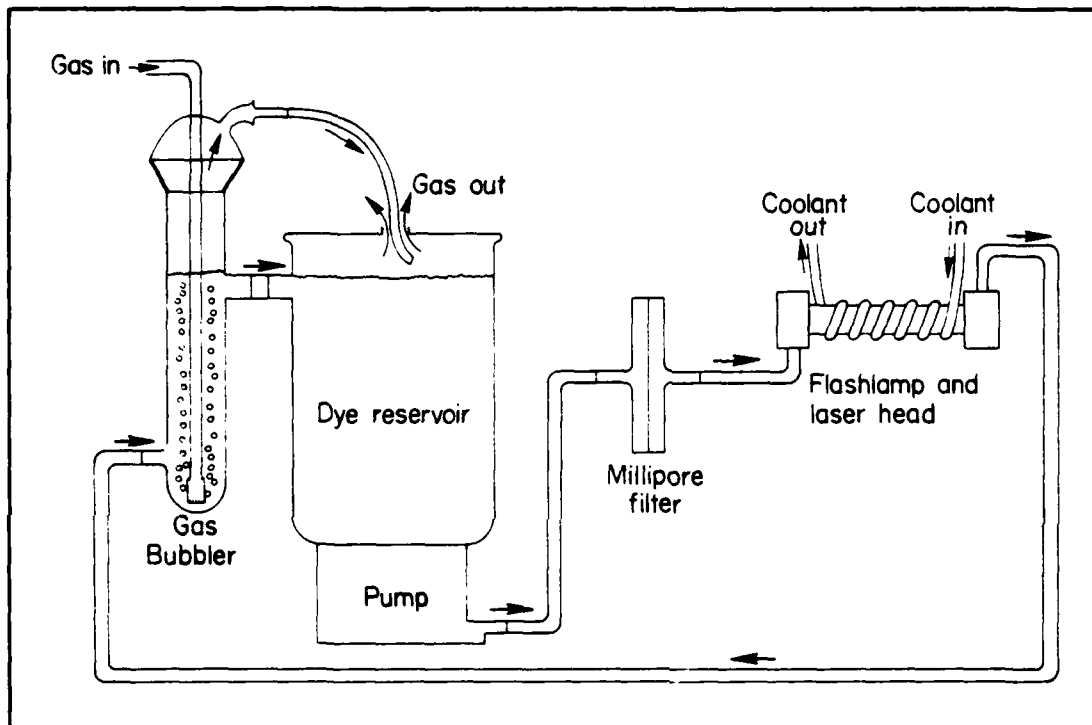FIGURE 9.   COMPARISON OF IRRADIATION CONDITIONS

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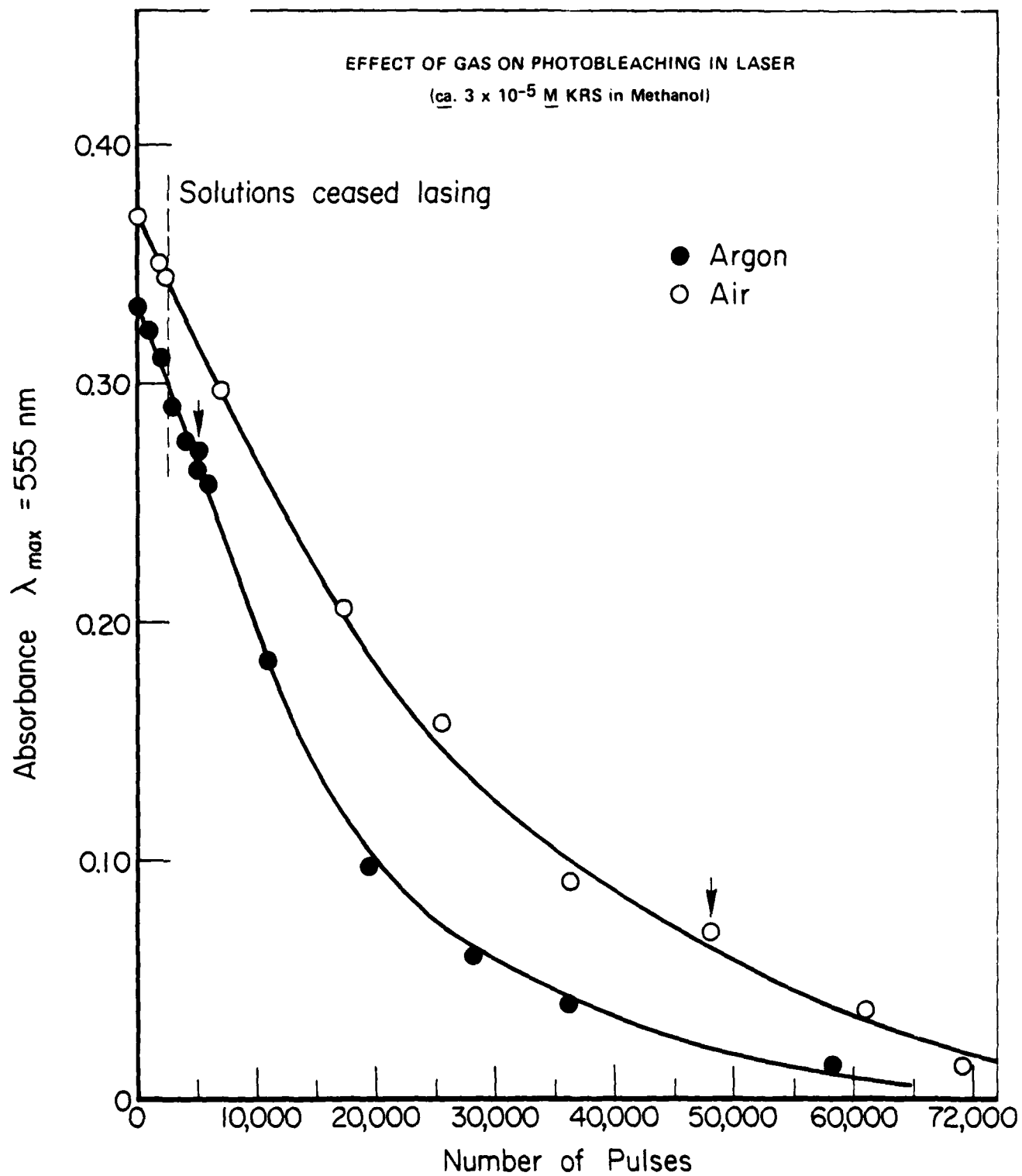FIGURE 10.   SCHEMATIC ILLUSTRATION OF
LASER FLOW SYSTEM

FIGURE 11. PHOTOBLEACHING OF FLASHLAMP-IRRADIATED KRS IN
METHANOL (ARROWS INDICATE SAMPLES WHICH WERE ALLOWED
TO STAND OVERNIGHT IN DARK).

effect has also been seen by Johnson, et al. [4] We can offer no explanation for this behavior at present, other than to suguest that some of the dye precipitates out of solution during its flow through the laser and is trapped on the filter disc, where it slowly redissolves upon standing, thus reversing the initial effect.

Thus, it is clear that while oxygen retards the rate of photobleaching by roughly an order of magnitude, it does so with an accompanying perturbation of the photochemical processes which occur. Taken together with the wavelength effects discussed earlier, these results point to the intermediacy of a reactive triplet excited state which is formed by preferential intersystem crossing from an upper excited singlet state. The preferential formation of triplet excited states from upper singlets rather than from the lowest excited singlet (S_1) is an unprecedented and somewhat exceptional process. This is because the vibronic relaxation of upper singlets to S_1 usually occurs so rapidly (typically, in a few picoseconds or less) that competing processes simply do not have time to occur. In the present case, the intersystem crossing from S_3, S_4, or S_5 must be very rapid indeed in order to compete with vibronic relaxation to S_1.

We also infer than the reactive state is the lowest triplet, T_1, because there appears to be no qualitative difference in degradation products as a function of wavelength. That is, the bleaching of KRS induced by irradiation at >500 nm, while very slow, appears to give rise to the same product mixture as that formed during the rapid degradation induced by irradiation with wavelengths below 300 nm. If upper triplet states were involved in the actual degradation reactions, one would expect the product distribution to vary as a function of wavelength. Finally, we have been able to sensitize the photodecomposition of KRS by the addition of benzil, a diketone which forms triplets with nearly 100% efficiency. The triplet energy of benzil is ca. 54 kcal/mole,[31] well above the 41 kcal/mole triplet energy of KRS.[24] Triplet-triplet energy transfer from benzil to KRS should therefore be rapid and efficient. It

is of interest in this context that the fluorescence lifetime of KRS in
methanol is wavelength-independent, and is the same (about 2.5 nsec)
whether the solution is excited at 530 nm or at 265 nm.[*] This is con-
sistent with the scheme proposed here, in which the absolute quantum
yield of fluorescence would be reduced under ultraviolet excitation,
while the lifetime of the fluorescent S_1 state would be invariant since
energy partitioning occurs in the upper singlet states, not in S_1.

Thus, we have discovered what appears to a unique triplet-state
degradation process which occurs preferentially by way of upper singlet
states. The reaction is quenched by oxygen, presumably with the concomi-
tant formation of singlet (^1g) oxygen, and by other triplet quenchers
such as cyclooctatetraene. We therefore infer that the difference in
product distributions obtained in the presence and absence of oxygen re-
flects the diversion of the photochemical reactions from the intrinsic -
triplet state reactions of KRS to the reactions of singlet oxygen or other
oxygen species, such as peroxides, with KRS and/or with the methanol
solvent.

Kinetics of Oxygen Quenching

To explore the kinetics of oxygen quenching in more detail, a
series of experiments were undertaken in collaboration with Prof. Michael
A. J. Rodgets and Dr. Barbara Lindig, of the Center for Fast Kinetics
Research at the University of Texas at Austin. This is a National
Institutes of Health National Resource Facility, and is made available to
the scientific community at no charge for collaborative experiments of
this type. The Center is equipped with a variety of computer-controlled
fast spectroscopy systems for the study of events on a time scale ranging
from microseconds to picoseconds.

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[*] We thank Prof. K. J. Kaufmann (University of Illinois) for
assisting us with this measurement.

Initial studies were carried out to confirm the measured fluorescence lifetime of KRS in methanol, and to establish firmly that the fluorescent singlet excited state (S_1) was not quenched by oxygen. The results of this study are summarized in Figure 12, which shows a typical fluorescence decay plot and the computer-generated first-order fit to the data. The decay curve, and the measured fluorescence lifetime of 3.2 nsec, are unchanged in the presence or absence of oxygen, thereby demonstrating conclusively that S_1 is not quenched. This confirms our previous observation that the fluorescence spectrum of KRS is unaffected by oxygen.

A subsequent series of experiments was then conducted to measure the quenching of KRS triplets by oxygen. This type of measurement is performed most conveniently by monitoring the population of triplet state molecules directly by observing the triplet-triplet absorption spectrum of the dye. While the triplet yield of KRS is so low (probably about 2-3%) that the triplet-triplet spectrum cannot be observed by simply irradiating the dye, it was found that triplet formation can be sensitized effectively by adding anthracene to the solution and exciting the anthracene with ultraviolet light (313 nm) produced by a pulsed nitrogen gas laser. Anthracene triplets formed during the pulse can transfer their energy by collision with KRS molecules in solution, producing KRS triplets in sufficient abundance for easy detection. The energies of the anthracene and KRS triplet states are different enough that there is no overlap of the triplet-triplet spectra. The actual spectra were measured by monitoring the absorption of the solution with a white light source, monochromator, and detector oriented at 90° to the exciting pulse.

The results so obtained are shown in Figure 13, which gives the measured triplet-triplet spectrum of KRS at several different delay times (in microseconds) between the excitation pulse and the monitoring of the absorption spectrum. It can be seen that the spectrum peaks broadly at around 610-640 nm, with a shoulder at about 700 nm. The intrinsic decay of the triplet-triplet spectrum in the absence of oxygen (nitrogen-
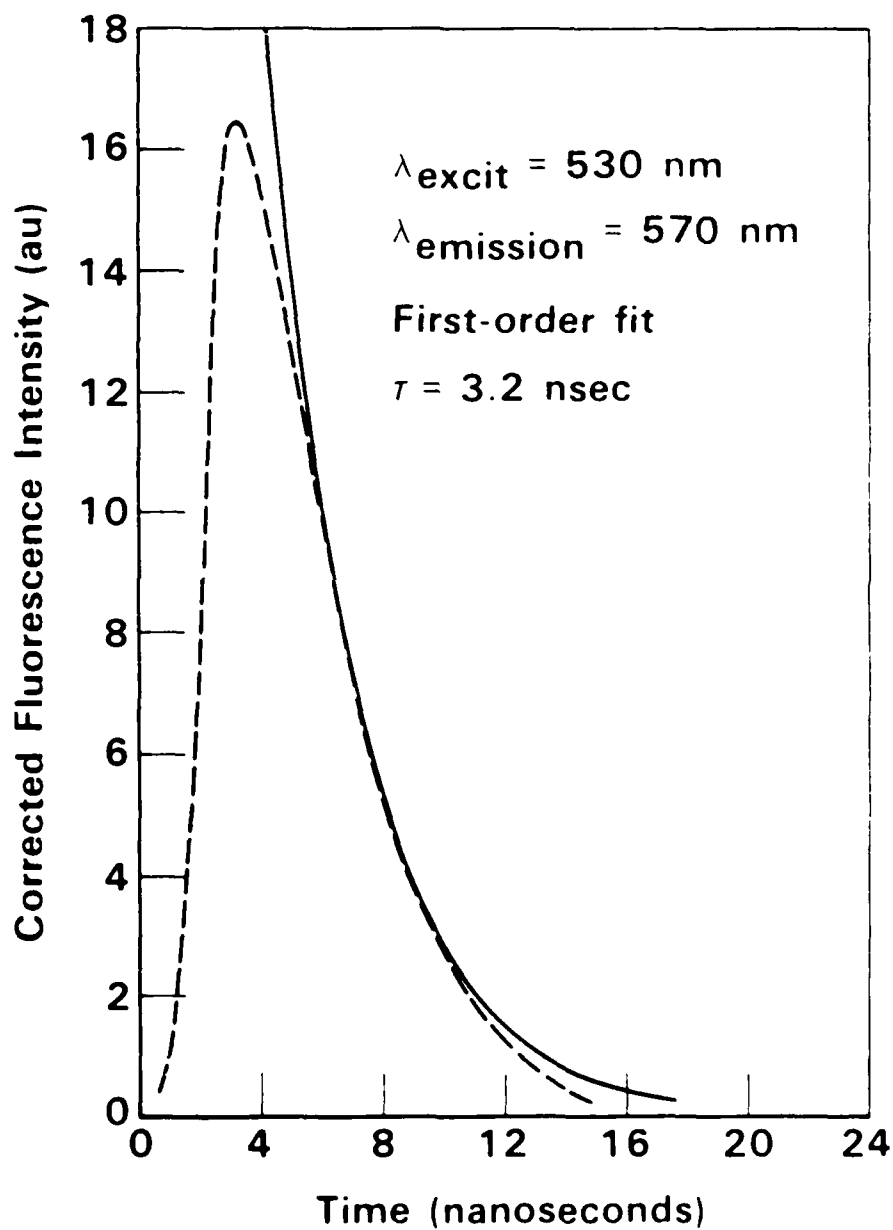
FIGURE 12. FLUORESCENCE LIFETIME OF KITON
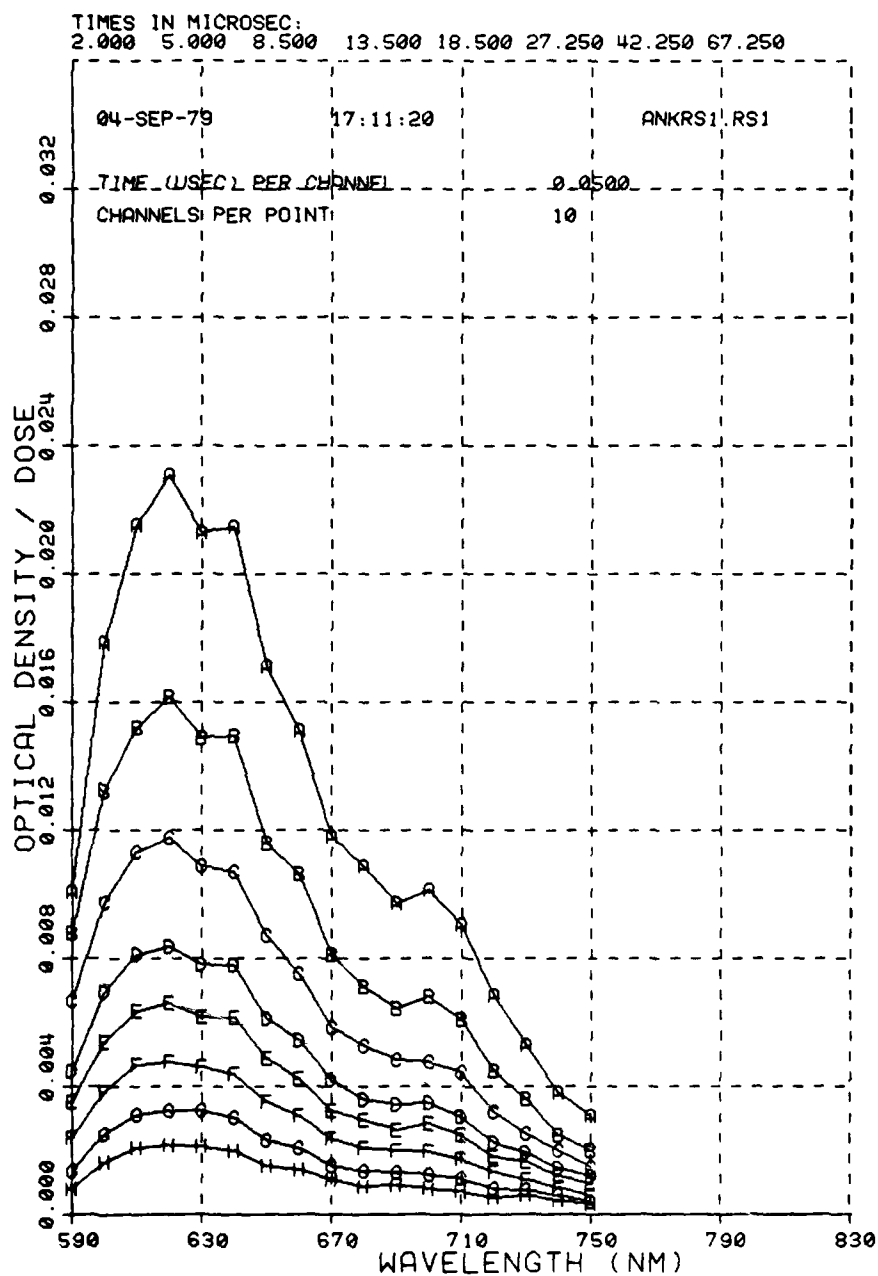RED S IN METHANOL

FIGURE 13. TRIPLET–TRIPLET ABSORPTION SPECTRUM OF KITON RED S

saturated) is best fitted as a mixed first- and second-order process, with a first-order rate constant of 1.6×10^5 sec^{-1} and a half-life of 4.4 microseconds.

Several experiments of this type were then carried out by Prof. Rodgers and Dr. Lindig, using varying concentrations of oxygen as determined by saturating the solution with precalibrated mixtures of oxygen and nitrogen prior to each measurement. The results of this work are summarized in Figure 14, which presents the rate of decay of the triplets as a function of oxygen concentration. While there is a good deal of scatter in the data, it is clear that oxygen does quench the triplets with modest efficiency. The measured (least-squares) quenching constant of 1.3×10^7 M^{-1} sec^{-1} is some three orders of magnitude slower than the diffusion-limited quenching constant for oxygen in methanol (ca. 10^{10} M^{-1} sec^{-1}); this may indicate a very low energy for T_1 of KRS, such that energy transfer from T_1 to oxygen to form $^1\Delta g$ singlet oxygen (23 kcal-/mole) is inefficient. Nonetheless, these results provide direct proof that oxygen quenches the triplet state of KRS but not the singlet excited state. Since oxygen also quenches the photodegradation process, we conclude that photodegradation must proceed via reactive triplet states which are formed preferentially by intersystem crossing from high-energy upper singlet states of KRS, not from S_1.

Discovery of a CCT Complex Between Oxygen and Methanol

An interesting sidelight to the oxygen effects on photodegradation has been the discovery of a previously unknown contact charge-transfer (CCT) complex between oxygen and methanol. This is manifested by the presence of intense end absorption in the ultraviolet spectra of methanol samples which are saturated with either air or pure oxygen, using argon-saturated methanol as a reference. For methanol which has been fully saturated with O_2, the absorption spectrum of the CCT complex begins at around 270 nm and rises steeply to shorter wavelengths, reaching
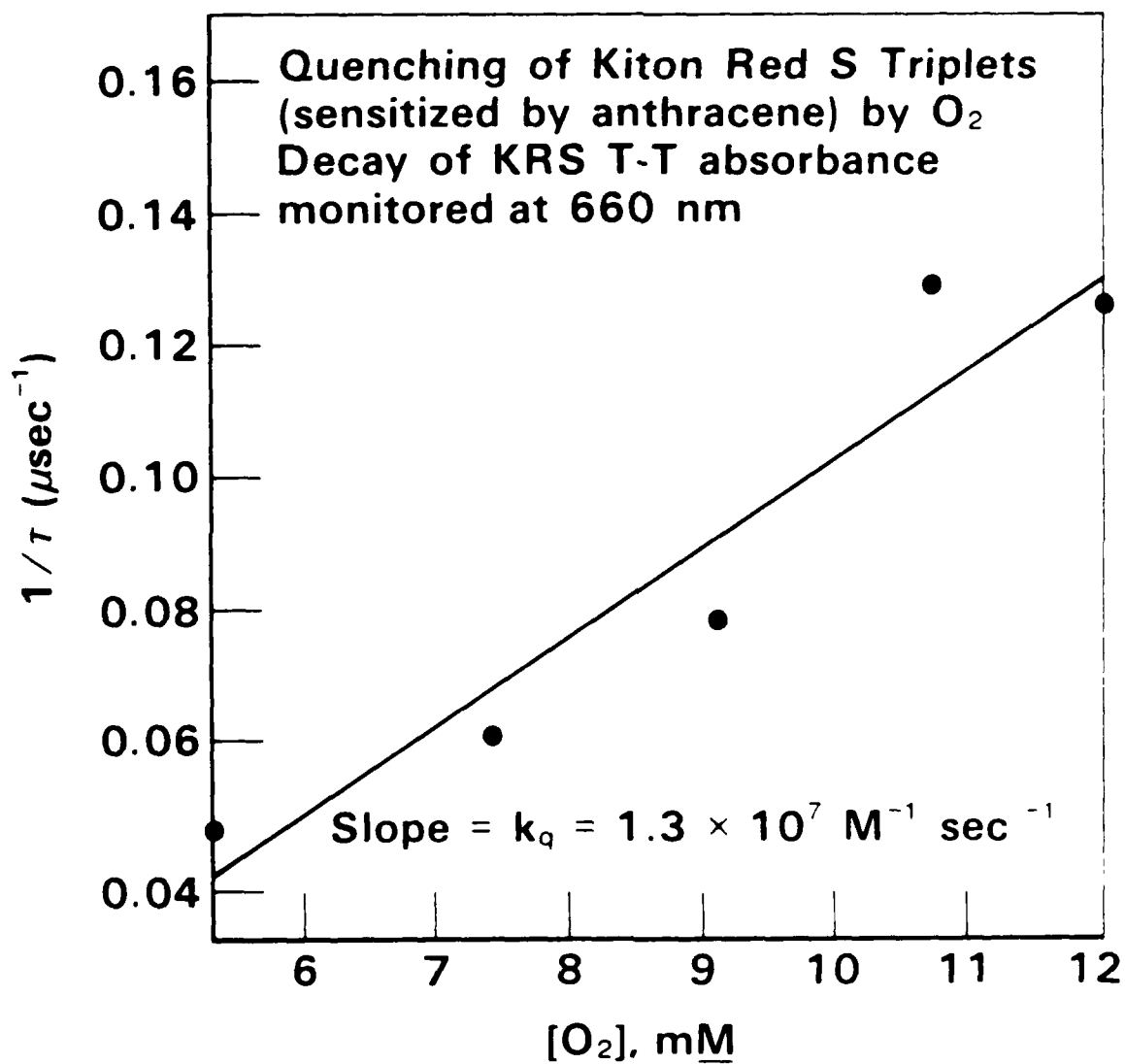
FIGURE 14.   QUENCHING OF KITON RED S
TRIPLETS BY OXYGEN

an absorbance of 1.0 (in a 1.0 cm cell) at 225 nm. Using more dilute
solutions of O_2, we have observed that the absorbance continues to in-
crease with diminishing wavelength down to the limit of our instrument's
wavelength range, at _ca._ 200 nm. The peak of the absorption band must lie
somewhat below 200 nm, but we have not been able to observe it.

The crucial observation, however, is that this absorption band
is readily and completely reversible; it can be made to appear or disap-
pear at will, simply by bubbling either O_2 or argon through the methanol
for a few seconds. Therefore, it cannot be the result of oxidation prod-
ucts derived from the methanol. Further, we find that this behavior does
not obtain in water; thus, the absorption band is not the result of mole-
cular O_2 alone, as gaseous O_2 absorbs well below 180 nm.[4]

The concept of contact charge-transfer complexes, in which the
two components form a loosely bound 1:1 complex upon collision in solu-
tion, was developed by R. S. Mulliken to explain the absorption spectra of
systems such as iodine in benzene.[32] In that case, gaseous iodine
vapor absorbs below 200 nm, while in benzene the absorption extends out
past 260 nm. The behavior we observe with the oxygen-methanol system is
fully consistent with this type of complex.

Because the wavelength range in which the O_2MeOH CCT complex
absorbs is the same as that which is responsible for initiating the
photodegradation, it is reasonable to inquire whether the complex may in
some way be responsible for the degradation of the dye. Were this the
case, however, it would be expected that the addition of O_2 to solutions
of KRS would result in an increase in the rate of photobleaching, as lit-
tle or none of the complex is present in solutions which have been purged
with argon. The fact that O_2 actually retards the photodegradation pro-
cess provides compelling evidence against a destructive role for the
complex.

We suggest, in fact, that the principal effect of the CCT com-
plex is to provide an internal filter which aids in retarding the photo-
bleaching process by absorbing far-UV light which would otherwise be ab-

sorbed by the dye. This role has been confirmed by experiments in which
an argon-saturated solution of KRS in methanol was irradiated with light
from the Elmac lamp which had been filtered through another quartz cuvette
containing either O_2-saturated methanol or argon-saturated methanol.
The photodegradation rate of the solutions irradiated through the
O_2-saturated methanol was reduced significantly - by a factor of 3 to
4-as compared to the solutions irradiated through argon-saturated meth-
anol. Since the retardation of photobleaching caused by O_2 in situ is of
the order of a factor of 10, it can be seen that the internal filter ef-
fect of the O_2-methanol CCT complex is comparable in magnitude to the
triplet quenching effect of dissolved molecular O_2.

Singlet Oxygen Effects

We have performed a number of experiments in an effort to eluc-
idate the importance of singlet ($^1\Delta g$) oxygen in the photodecomposition
of Kiton Red S. These include both attempts to induce reactions of KRS
with externally-generated singlet oxygen, and experiments designed to
probe the efficiency of KRS as a sensitizer of singlet oxygen.

In the first series of experiments, both rose bengal and methy-
lene blue were used as singlet oxygen sensitizers in methanol solutions
with Kiton Red S. These irradiations were performed with the Eimac 150-
watt xenon arc lamp and either a Corning CS3-72 cutoff filter (for rose
bengal) or a Corning CS2-59 cutoff filter (for methylene blue) to ensure
that only the sensitizer, and not the Kiton Red S, would absorb any light.
Prolonged irradiation (up to several hours) under these conditions pro-
duced no detectable change in the absorption spectrum of the solution,
indicating that no change occurred in the Kiton Red S. To confirm that
singlet oxygen was in fact being produced, these experiments were repeated
with the Kiton Red S replaced by 9,10-diphenylanthracene, a known singlet
oxygen acceptor. The diphenylanthracene disappeared rapidly under these
conditions. Thus, it appears clear from these results that Kiton Red S

reacts only slowly, if at all, with singlet oxygen in solution under these conditions.

Subsequent experiments, designed to study the reactions of Kiton Red S in methanol with singlet oxygen generated completely externally to the reaction vessel, were unsuccessful. In these experiments, we hoped to make use of a variation on the heterogeneous sensitization technique described by Kerns.[33] A "fluidized-bed" reactor was prepared by partially filling a small glass tube with silica gel which had been coated with rose bengal. This was then irradiated with a 450-watt Hanovia mercury arc lamp while a mixture of ca. 1-2% oxygen in helium was blown through the tube. In principle, singlet oxygen should be formed at the irradiated gas-particle interface and carried out of the tube by the helium flow. The gas emerging from the tube was conducted by teflon tubing into a darkened flask containing a solution of rubrene (another well-known singlet oxygen trap[33]) in toluene. This system was chosen because it provides a very sensitive indicator of the presence of small amounts of singlet oxygen. Numerous experiments were performed with this system, using various conditions of flow rate, gas composition, and so on. No reaction of the rubrene could be detected after several hours under any of the conditions used. Presumably the singlet oxygen was formed in low yield, and was quenched rapidly either by the carrier gas, or by components in the reactor tube or the teflon tubing.

A final set of experiments was conducted in collaboration with Major William McDermot and Captain David Ellis, of the Chemical Laser Group at Kirtland AFB, New Mexico. In these experiments, samples of both Kiton Red S and rhodamine B were impregnated on highly pure filter paper (which had been previously washed with methanol) and exposed to massive (several hundredfold) mole excesses of singlet oxygen produced in the chemical laser generators at Kirtland. Solutions could not be used in these experiments, because the entire singlet oxygen generating system was maintained under vacuum during their experiments.

When the filter papers were then analyzed by comparing their infrared spectra obtained before and after exposure to singlet oxygen, virtually no change could be observed in the samples of KRS and only minor changes (less than 1% change in the intensities of the major bands) in the rhodamine B samples. Similarly, no changes could be observed in the visible-UV spectra of solutions of the dyes eluted from the filter papers. We therefore conclude that in the absence of solvent (either methanol or water) these xanthene dyes react at a negligible rate with singlet oxygen. The role of solvent is still unclear at this time, as we have observed that thin films of solid KRS do in fact degrade upon irradiation in air.

Peroxide Effects

A final brief series of experiments was carried out to explore the effects of adding hydrogen peroxide, in the thought that the singlet oxygen formed by triplet quenching may react with solvent to form peroxide species of some type. We find that the addition of only 75 microliters of 30% aqueous hydrogen peroxide to a 2 cm cylindrical cell of air-saturated KRS in methanol (which contains about 5 ml) is sufficient to cause a threefold increase in the rate of photodegradation, despite the fact that the peroxide absorbs strongly in the UV. Thus, it may be that hydroxy radicals or hydroperoxide radicals formed by cleavage of the peroxide may be the key reaction intermediates in the photodegradation process. If this is true, then the addition of radical-scavenging reagents such as polyenes or metal chelates may help to prolong the lifetime of the dye.

Analysis of photodegradation Products

As was noted earlier in this Report, the analysis of volatile photodegradation products by gas chromatographic techniques was hampered by the complexity of the product mixtures, with up to 15-20 products being detected depending on the irradiation conditions used. Little further insight could be gained by UV-VIS, IR, or NMR analysis of the product mixtures; as the dye bleached during irradiation, the spectra seemed to

simply disappear with it. Only a small increase in featureless end absorption in the UV spectrum provided any indication that new products were being formed. In oxygen-saturated methanol, however, the IR spectrum did seem to indicate the rapid loss of the diethylamino end groups of the dye during the early stages of the irradiation, as though they were being cleaved off or attacked by hydroxyl radicals to give α-hydroxyamino groups. This behavior is manifested by the rapid loss of the IR band at 7.5 microns, which is characteristic of the alkyl C-N stretch.

Accordingly, an effort was made to analyze the non-volatile photoproducts remaining in the solutions by means of HPLC, using (after some trial and error) a reverse-phase column with 28% aqueous acetonitrile containing 0.15 $\underline{M}$ triethylammonium bicarbonate (TEABC, ion-pairing buffer) as the eluent. Optical detection at 254 nm was used. The results of these studies are shown in Figures 15 and 16. It can be seen that a number of new products have formed, and that the amount of KRS has decreased substantially relative to the amount of minor component. A series of these chromatograms, taken at different times during the irradiation, suggests that the amount of minor component stays unchanged during the irradiation, while the KRS peak declines and the other peaks grow in. However, it is still not known whether the minor component actually lies on the photodegradation pathway or not. It has not proven possible for use to acquire preparative samples of the degradation products in amounts sufficient for further analysis, and their identity, unfortunately, remains unknown.

Finally, in response to the claim by Mostovnkiov, et al, [22] that carboxylic acids formed during the photodegradation of rhodamine dyes serve to catalyze the degradation process, we have sought carefully to detect such acids in our product mixtures, and to test for catalysis of the photobleaching reactions by the deliberate addition of selected acids to several irradiation experiments. Our results in both categories have been consistently negative. We find no evidence for the formation of free carboxylic acids such as formic acid or acetic acid under our conditions
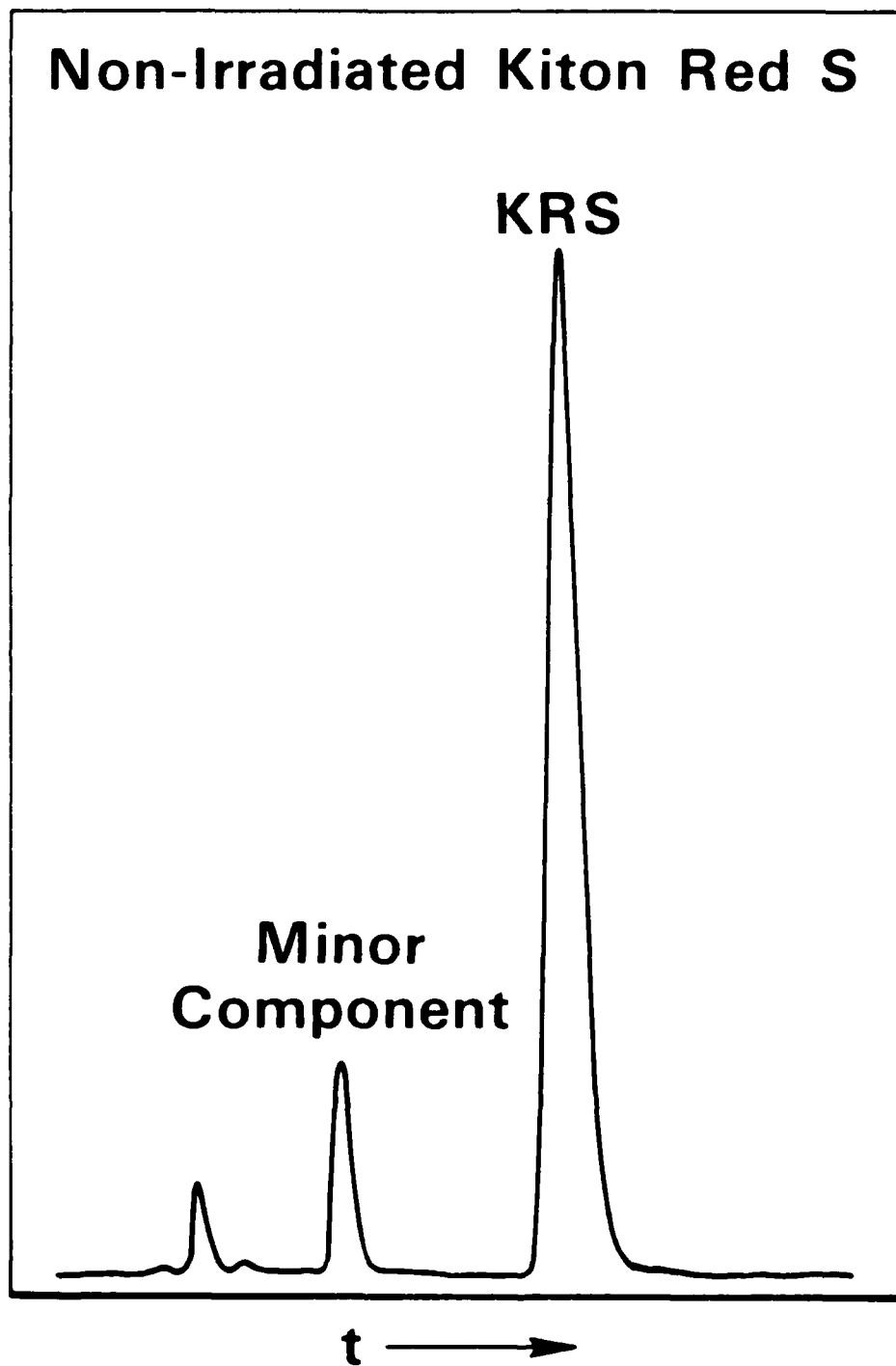
FIGURE 15. HPLC CHROMATOGRAM OF KITON RED S
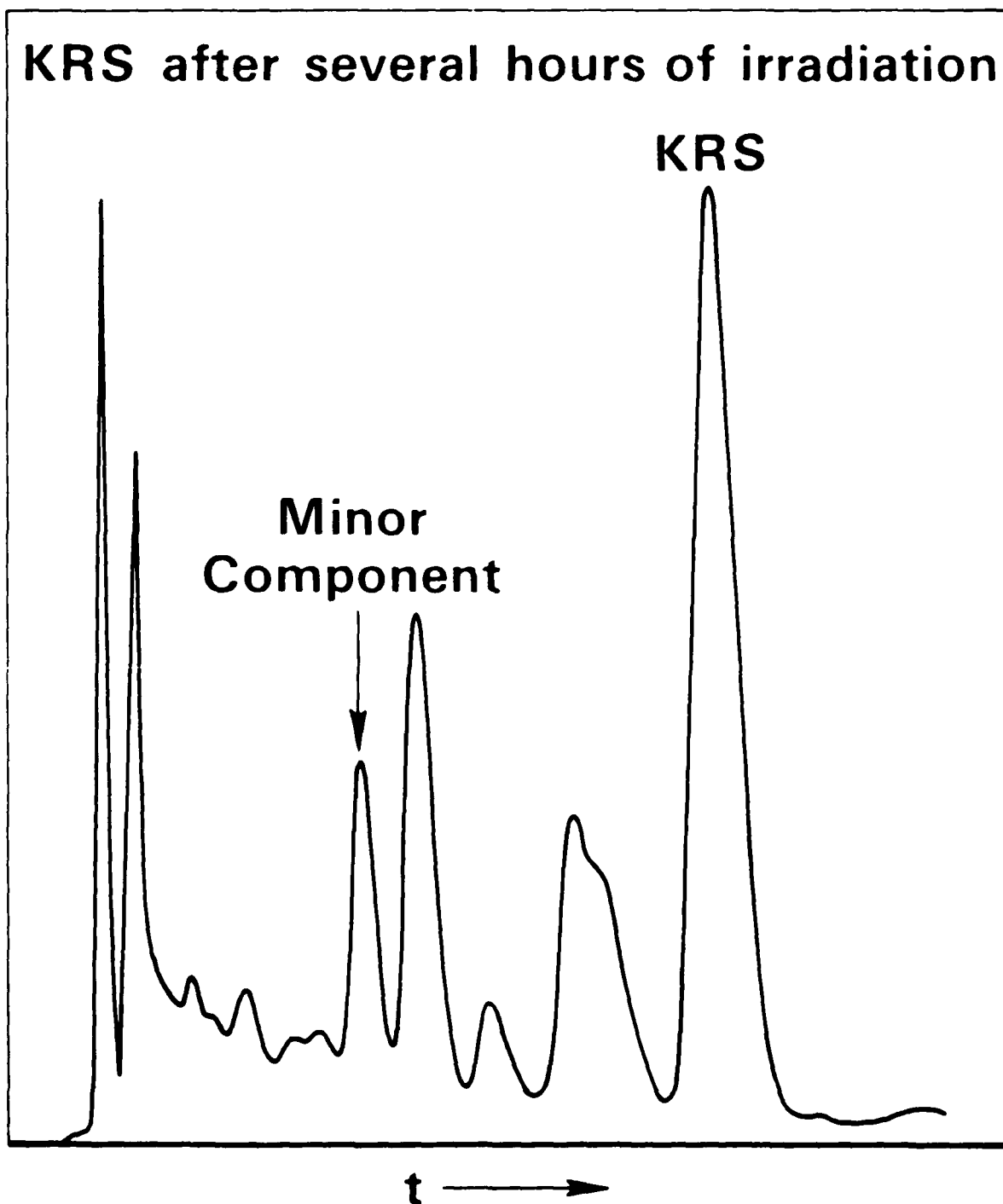IN METHANOL PRIOR TO IRRADIATION

FIGURE 16. HPLC CHROMATOGRAM OF KITON RED S IN
METHANOL AFTER IRRADIATION FOR SEVERAL HOURS

of irradition in methanol, nor did the addition of acetic acid, hydro-
chloric acid, or pyridine have any detectable effect on the rate of
photobleaching.

Similarly, both we and the group at Wright-Patterson Air Force
Base[4] have observed that (a) the lasing ability of KRS solutions dete-
riorates far more rapidly than the photobleaching process occurs, in that
lasing frequently ceases when the absorbance of the visible band has
dropped by less than 10%, and (b) partially degraded solutions frequently
recover some of their lasing ability upon being allowed to stand for sev-
eral hours in the dark, although the visible absorbance band shows no such
behavior. Thus, there appear to be photoproducts which interfere with
stimulated emission under the conditions of high light intensity which
obtain within the lasing solution, but which do not affect the visible
chromophore of the dye. Pre-irradiation of the methanol solvent alone
does not accelerate the photodegradation of the KRS solutions, however.
These effects are not understood at present, and await the successful
elucidation of the photodegradation products.

Proposed Mechanism of Photodegradation

We hypothesize that the observed photobleaching behavior de-
scribed above is a direct consequence of the electronic structure of
xanthenes, and of KRS in particular. Jakobi and Kuhn[34] have shown that
the long-wavelength (visible absorption band of the xanthene dyes is
long-axis polarized; that is, the transition dipole is oriented along the
long axis of the molecule. This is consistent with the charge-transfer
nature of this electronic transition. The ultraviolet absorption bands
are short-axis polarized, however, with the transition dipole oriented
along the short axis of the molecule.[34] These relationships are de-
picted schematically in Figure 17, below. The point to be made here is
that excitation with visible light should have a relatively small effect
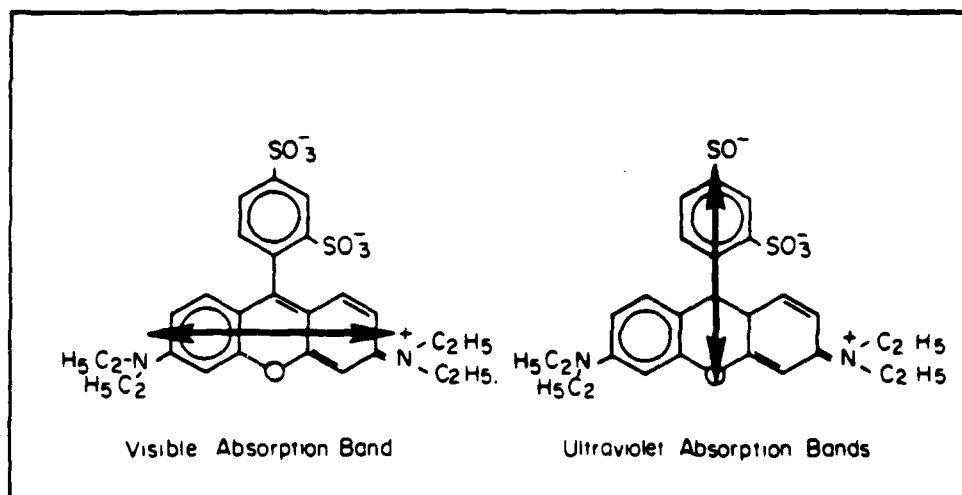on the electron density distribution of the 9-bis-sulfonylphenyl sub-

FIGURE 17.   TRANSITION DIPOLE ORIENTATION FOR KITON RED S

stituent, since the change in electron distribution occurs primarily along the xanthene moiety of the molecule. Excitation with ultraviolet light, on the other hand, should cause a large pertubation of the electron distribution of the 9-bis-sulfonyphenyl substituent, giving rise to excited singlet states (S_3, S_4, S_5) which have enhanced electron density on the 9-bis-sulfonylphenyl group. It is our hypothesis that these upper singlet states, and particularly S_4 and S_5 (which are accessable with light of wavelengths below 250 nm), possess concentrations of localized electron density at the ortho and para positions of the ring, as illustrated schematically below. This means that the possibilities for spin-orbit coupling with the heavy sulfur atoms at these positions should be enhanced significantly in these states, but not in S_1. If this is the case, it provides a ready explanation for the observed behavior, as intersystem crossing would be facilitiated by the enhanced spin-orbit coupling which is "turned on" only in the upper singlet states.
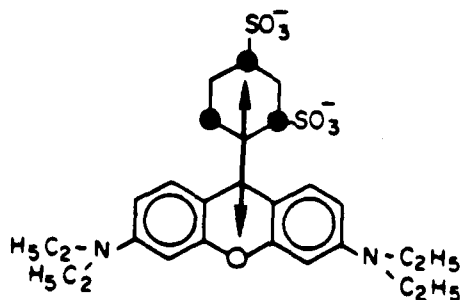
Quantum-Mechanical Calculations

To explore the validity of this hypothesis, a series of SCF-CI quantum-mechanical calculations employing the PC/LO formalism[35] have recently been performed for us by the Computational Chemistry Group at Battelle. These calculations have provided estimates of (1) the electron (charge) density at each atom of KRS in the ground state and in all of the singlet excited states which can be populated with visible or ultraviolet light, (2) the wavelength, energy, and oscillator strength of each transitions, and (3) the molecular orbitals which contribute to each transition. From these data, it has been possible for us to follow the flow of electron density on key atoms of KRS as it is excited from the ground state to the upper singlet states, and thus to estimate the extent to which enhanced spin-orbital coupling may contribute to triplet formation from each state, as we have suggested. The analysis of these calculations, while complicated by the large number of states involved in such a complex molecule as KRS, supports our hypothesis that many of the upper singlet excited states which lie above 120 kcal/mole (240 nm excitation) contain significantly more electron density on the carbon atoms of the 9-phenyl group which lie ortho and para to the xanthene ring system. Because these are the atoms which carry the sulfonic acid groups in KRS, and the carboxyl group in rhodamine B and several other xanthene dyes, it is entirely plausible that our proposed mechanism obtains. Clearly, the proximity of the heavy sulfur atoms to the atoms bearing increased electron charge increases the probability of enhanced intersystem crossing via enhanced spin-orbit coupling (the heavy-atom effect), thus giving rise to more rapid triplet formation from these high-lying states than from the lower singlet excited states. While these results are of course not conclusive, because of the inherent uncertainties in calculations of this type, they provide additional support to the mechanism we have proposed.

We thus envision that the photodegradation process proceeds by way of the mechanism shown schematically in Figure 18, below. This is an unprecedented process of considerable theoretical interest, for it represents the first known example of a molecule in which intersystem crossing proceeds more rapidly from upper singlet states (indeed, competetively with vibronic relaxation) than from the lowest singlet excited state. It would be of significant fundamental importance to study other, related xanthene dyes with this mechanism in mind, so as to probe the limits of the structural features which give rise to this behavior.
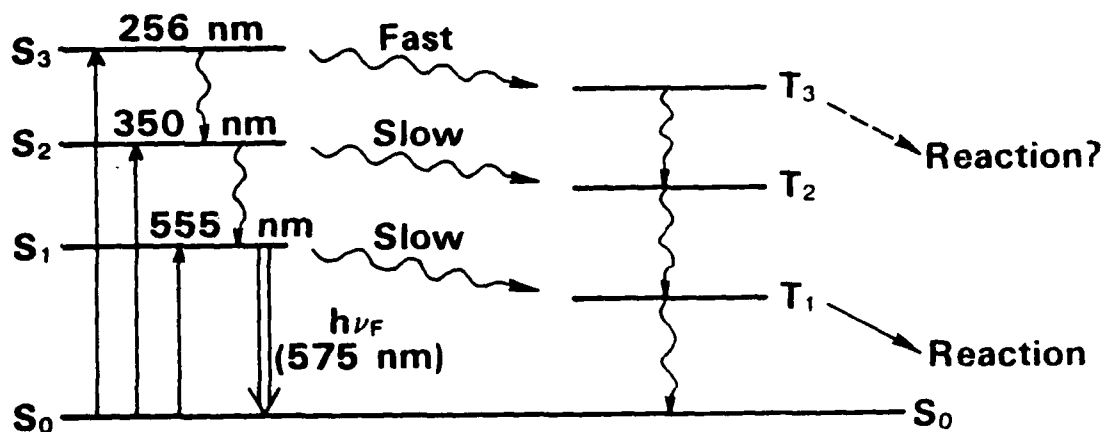
FIGURE 18. SCHEMATIC ENERGY-LEVEL DIAGRAM FOR THE PHOTOCHEMICAL DECOMPOSITION OF KITON RED S

Postulated Chronology of Photodegradation

As noted before, the rapid loss of the C-N stretch band at 7.5 microns in the infrared spectrum suggests that the diethyl amino groups are being modified early in the degradation process, either by cleavage (de-ethylation) or by α-hydroxylation of the ethyl groups. This is a plausible first step in the decay process, and one which should have minimal impact on the conjugated ring system (and thus on the visible absorption spectrum). Of the two possibilities, hydroxylation seems the more likely because no progessive blue shift is observed as would be expected for successive cleavage of the ethyl groups.

We also note that in the intrinsic (argon-saturated) photobleaching of KRS, the visible absorption band exhibits a slight blue shift as it fades, with the concomitant formation of foul-smelling mercaptans. Thus, we may postulate that the reduction of the $R-SO_3^-$ groups to R-SH groups constitutes the second step of the photobleaching process. This may or may not be accompanied by loss of the 9-phenyl substituent. Finally, the remaining molecule seems to fragment completely in the final stages of photobleaching, with complete loss of aromatic electronic structure.

Thus, we may postulate that the intrinsic photobleaching of KRS occurs in at least three distinct phases, exclusive of any effects of singlet oxygen. These are depicted schematically below in Figure 19. We note that the formation of mercaptans could be linked to attack on the end groups if the molecules form dimers or higher aggregates in solution, but we have no data on this point at present. The chronology suggested in Figure 19 should be considered as a plausible sequence of steps, not a rigorous interpretation of the degradation sequence. In that vein, it may be viewed as a rational starting point for future, more detailed studies of the photodegradation products.
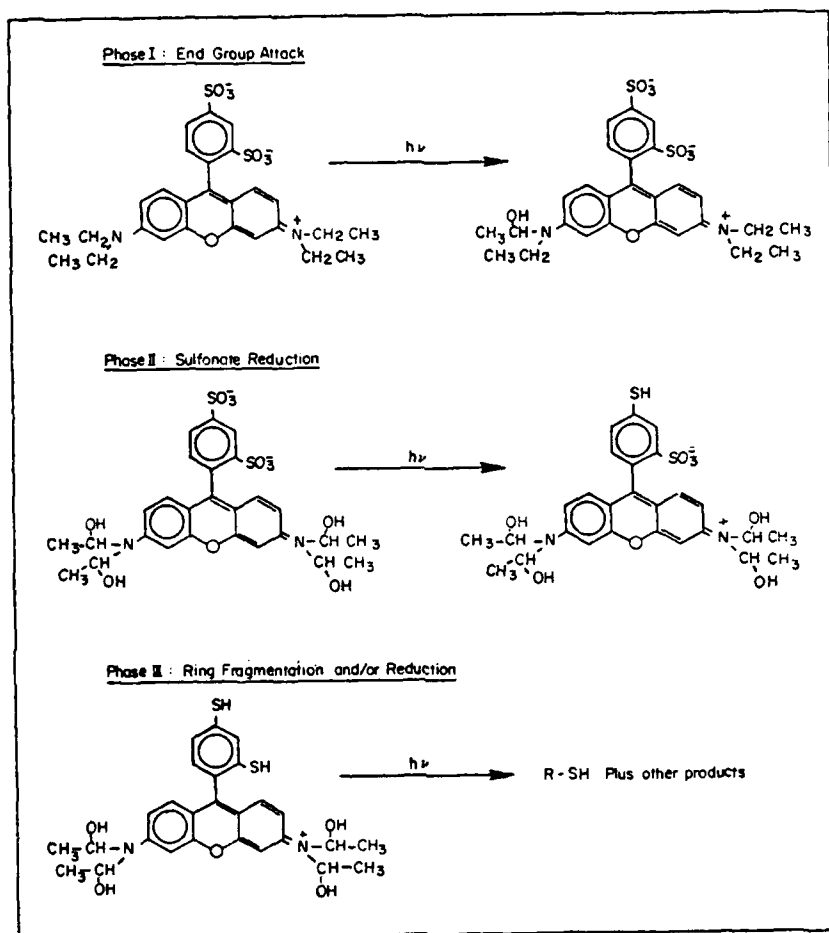
FIGURE 19. POSTULATED CHRONOLOGY OF PHOTODEGRADATION
OF KITON RED S

SUMMARY

In summary, the research performed in the course of this program has led to the discovery of an unprecedented excited state pathway for the photodegradation of Kiton Red S, and has permitted us to postulate a tentative chronology for the first stages of the photodecomposition process. These findings also permit us to suggest that the stability of xanthene laser dyes could be improved markedly by:

- eliminating the far-UV wavelengths below 240 nm by means of a suitable cut-off filter (which could be achieved most easily by making the laser tube from a glass composition having the desired absorption characteristics), and

- incorporating efficient triplet quenchers other than molecular oxygen (to avoid the potential problems associated with peroxide formation) or, alternatively, using air-saturated solutions with efficient free-radical scavengers added to prevent peroxide-derwed radicals from attacking the dye.

In addition, we have discovered both a novel CCT complex between oxygen and methanol, and a previously unsuspected impurity in commercial laser grade Kiton Red S. Finally, we have confirmed the findings of the group at Wright-Patterson AFB that lasing ceases when solutions of KRS in methanol have photobleached by less than 10 percent. The details of this process, and of the photodegradation products responsible for it, remain unknown at present, and could form the basis for continued research in this field.

KEY PROJECT PERSONNEL

The research performed during this project has been directed by
Dr. Robert E. Schwerzel (Principal Investigator), with the assistance of
Ms. Nancy A. Edie. Ms. Edie has also been responsible for performing the
bulk of the experimental research during this program, including the
photochemical irradiations and the visible-UV and fluorescence spectro-
scopic measurements.

Analytical assistance with the project has been provided by a
number of Battelle scientists. Infrared spectra have been recorded and
interpreted by Mr. Robert J. Jakobsen, Ms. Rachel L. Barbour, Mr. Charles
J. Riggle, and Ms. E. Jo Brewer. Nuclear magnetic resonance spectra were
provided by Dr. John R. Nixon, Mr. Thomas R. Householder, and Dr. Pauline
A. Clarke. Gas chromatography data were recorded by Dr. J. Scott Warner
and Mr. Thomas H. Danison, while HPLC separations were performed by Dr.
John R. Nixon, Dr. Ralph M. Riggin, Ms. Corrine Howard, and Ms. Sheila M.
Graham.

Technical assistance with a variety of experimental details, and
assistance with the repair of occasional instrument malfunctions, was
provided by Mr. Fred R. Moore. Additional assistance with various optical
components, including the pulsed dye laser, was provided by Dr. Carl M.
Verber and Mr. Nile F. Hartman. Expert computational assistance with the
PCILO quantum-mechanical calculations was provided by Dr. Rodney J.
Bartlett and Dr. Lynn T. Redmon.

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PUBLICATIONS

Two publications based on the above results are in preparation, and will be submitted shortly now that our final confirmatory experiments have been carried out. In addition, papers based on this research were presented at the 175th ACS National Meeting, in Anaheim, California (March, 1978); at the 11th ACS Central Regional Meeting, in Columbus, Ohio (May, 1979); at the Gordon Conference on Photochemistry, held at Proctor Academy, New Hampshire (August, 1979); and at a Battelle-sponsored Conference on Photochemistry, in Columbus, Ohio (October, 1980).

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